

## THE AGE OF OIL

BIRTHDAYS in the family are great fun. They are an excuse for the young to overeat and a licence for the old to maunder in reminiscence. The young want more birthdays to become less young, the old want fewer to be less old. Industries do not have birthdays because their birth is usually a protracted agony of travail and it is not easy to see just when the infant is viable. But industries do have jubilees. It is just one hundred years since the first successful oil well was drilled in Pennsylvania; and British Petroleum is fifty years old. It was on May 26th, 1908 that the first successful oil strike was made in the Near East, in Persia: 'I have the honour to report that this morning at about 4 a.m. oil was struck in the No. 1 hold at a depth of 1180 feet . . . Particulars, re gravity and quantity of oil flowing will follow but unless I get this away at once, I shall miss the post'<sup>1</sup>.

Oil, commercial oil may be animal, mineral or vegetable and over a hundred years ago the animal and vegetable oils predominated. There is indeed a considerable industry to this day based on animal oils and there are vast enterprizes built on the commercial exploitation of vegetable oils and their myriad applications from margarine to cosmetics. Nevertheless to most of us nowadays the word oil really means mineral oils, the petroleum industry with its pictures of oil derricks and tankers, of petrol stations and diesel buses. It means politics and pipelines, it means peace and plenty; it also means wars and rumours of war. The industry represents today probably the single largest, international, commercial undertaking of man for the annual turnover is of the order of £9000 million which makes most national budgets look small. The lunch-time traffic in London wastes an amount of money in the form of 'oil' which would make an Elizabethan chancellor of the exchequer wince. If we did not take it for granted because we are so used to it, it would make us wince, instead of merely making us cantankerous.

The advent of nuclear power has led to much comment on the place and the passing phase of the fossil fuels. In the next hundred years the conviction will grow that the true industrial place of petroleum is not as a fuel but as a primary raw material of an expanded chemical industry. This is true enough but should not conceal the quite staggering changes, domestic changes and industrial changes, brought

about by the oil industry. In the early days of British Petroleum the influence of Lord Fisher on behalf of the Admiralty was real and indeed vital. Now the tonnage of the tanker fleet of British Petroleum is of the same order as that of the Navy.

The advantages of oil are obvious. Though found with difficulty, it can be mined relatively cheaply. It is easily handled for it can be transported by tanker or by pipe-line. It can be processed for use in units as small as a motor bicycle or as large as a power station. There are today many alternative fuels; coal, hydrogen peroxide, oxygen, boron fuels, fission fuels. And power is the basis of civilization, the sinews of society are the horse power at the control of the workman. No wonder politics is involved for the sources of industrial power will remain of vital concern in the science and art of government until mechanical power can be purveyed as a cheap service and the needs cannot be used as weapons. Then, and only then, will it be possible to make a relative assessment of coal, gas, oil, fission and fusion in terms of capital outlay and the mechanical equivalent of heat.

In the valley of the Euphrates bitumen has been used for five thousand years and the 'Eternal Fires' which burned in the days of Nebuchadnezzar the King still burn today. In less than fifty years these 'fires' have not only been tapped but their bottled heat has been distributed all over the globe. It has been fractioned and refined, and to each fraction a purpose has been assigned; with every year the purposes grow. Petroleum has been called 'liquid gold'. Certainly it is wealth, it is power, it is a medium of exchange. It is a fuel, a lubricant, a chemistry. It is also a revolution. It is easy and natural to become impatient with policy makers and to draw attention to the obvious need for a reasoned fuel policy, a policy of development, a policy of investment. In the last fifty years coal has been eclipsed by oil and both are threatened—if that is the right word—by nuclear fission fuels. The fundamental human need of mechanical power can now be stated in terms of nuclear fusion. Revolution seems to be a pale word to use of such eruptive upheavals in human affairs but the dramatic suddenness and almost reckless rate of development emphasise the urgency. Of recent years, there has been in this country evidence of an 'I love you, I love you not' vacillation towards oil. Certainly these problems are not merely technological, that is what makes their resolution the more difficult and the more urgent.

<sup>1</sup> *Adventure in Oil* by HENRY LONGHURST (London: Sedgwick and Jackson (1959), 21s)

# COOPERATIVE MAGNETISM IN OXIDE STRUCTURES

## Part I—Antiferromagnetism and Ferromagnetism

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Some introductory remarks on the fundamentals of magnetism are followed by a discussion of the antiferromagnetic and ferromagnetic properties of certain oxide systems. A brief account is given of the current theories of indirect magnetic exchange interaction. Part II, which will appear in the next issue of *RESEARCH*, deals with the ferrimagnetic properties of other oxide systems.

THE PHENOMENON of cooperative magnetism in oxidic and related compounds has attracted in recent years the increased attention of chemists, crystallographers and physicists. Much of the interest is in connection with the rapid growth of technical application of certain of the compounds in the fields of radio, television, microwave electronics *etc.* To the theoretical chemists and physicists, however, the whole subject is of immense interest in that it extends the range of magnetic exchange interaction to structures that are diluted by non-magnetic ions.

The aim of these articles is to discuss the origin of antiferromagnetism, ferromagnetism and ferrimagnetism in the various classes of compounds, mainly oxides, that contain metal ions of the first transition series or of the rare earths. It is not possible to dwell deeply on the theoretical aspects of magnetic exchange, nor to describe the individual methods employed in the preparation of the compounds; this information may be found in the reference literature. Moreover, the technical importance of some of the compounds is mentioned only where it can aid the general discussion.

### Theoretical Principles

Before discussing the details of cooperative magnetism in essentially ionic compounds the fundamentals of magnetism will be summarized.

The extent to which a substance is magnetized in the presence of an external field  $H$  is measured by its intensity of magnetization  $I$  per unit volume. The ratio  $I/H$  is called the magnetic susceptibility  $\chi$  per unit volume.

The origin of magnetism in an atom or molecule lies in the motions of the extranuclear electrons. Both orbital and spin motions give rise to magnetic moments which tend to be oriented in the presence

of an external field. When all the electrons occur in balanced pairs in the various shells there is no resultant spin moment and the substance is termed *diamagnetic* and is characterized by a very small negative magnetic susceptibility. In other substances that contain unpaired electrons there exist permanent magnetic moments at individual atomic sites. Unpaired electrons have both spin angular momentum  $s$  and orbital angular momentum  $l$  and these combine to give a resultant magnetic moment, but the way in which they couple together is very important. It is convenient for the moment to neglect the orbital contribution to the magnetic moment—this is often almost completely quenched by the crystalline field in the lattice—and to consider that the moment arises entirely from the spin angular momentum.

If the individual atomic moments are uncoupled to one another their orientation in the absence of an external field is random; such a substance is termed *paramagnetic*. The effect of an external field is to cause partial alignment of the spins in the direction of the field; but except with very intense fields at temperatures close to absolute zero the alignment is far from complete. This is because thermal effects of vibration, rotation and translation strongly oppose the alignment. For a typical paramagnetic substance  $\chi$  is of the order of  $10^{-4}$  e.m.u.

When paramagnetic ions occur sufficiently close together in a lattice they may interact with one another, by mechanisms to be discussed later, so that their electron spins all lie parallel to a given direction even in the absence of an external field. This cooperative behaviour is known as *ferromagnetism* and is characterized by large positive values of  $\chi$ . In the unmagnetized state the macroscopic magnetization of a ferromagnetic substance

is zero because the parallelism of the atomic moments occurs only within certain regions of the crystal called Weiss domains which are not oriented with respect to one another. The action of an external field is

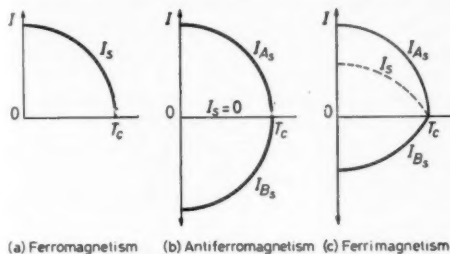


Figure 1. Schematic representation of behaviour of saturation magnetization with temperature ( $I_s$  is resultant magnetization) and of the spin moment orientations for the three types of cooperative magnetism

to align the domain moments in the direction of the field against certain forces associated with the crystal structure, the direction of stress in the lattice and with the physical shape of the material. Although relatively small magnetic fields tend to produce magnetic saturation, complete parallelism of atomic moments is only possible at 0°K when thermal disorder is absent. With increasing temperature above 0°K the observed saturation magnetization decreases, falling to zero at the Curie temperature  $T_c$  (Figure 1a). This represents the temperature at which the thermal energy overcomes the aligning energy of the exchange interaction. Above the Curie temperature a ferromagnetic substance assumes many of the characteristics of a paramagnetic material but the exchange interaction energy continues to play a role.

A second type of cooperative magnetic interaction which leads to an antiparallel orientation of the moments of nearest neighbour atoms or ions was proposed in 1932 by L. NÉEL. This phenomenon, known as *antiferromagnetism*, is characterized by positive susceptibilities of the order of  $10^{-4}$  e.m.u. which, in common with other properties such as specific heat and thermal expansion, exhibit a  $\lambda$ -type peak at a critical temperature called the Néel temperature  $N_c$ . This temperature is analogous to the ferromagnetic Curie temperature.

The crystal structure of an antiferromagnetic substance is such that the magnetic atoms can be divided into two interpenetrating sublattices. Magnetic

atoms on sublattice *A* have nearest neighbours on sublattice *B* only, and vice versa. The saturation magnetization versus temperature curve for each sublattice is similar to that of a simple ferromagnetic, as illustrated in Figure 1b, but the net magnetization is zero. Above the Néel temperature an antiferromagnetic substance behaves paramagnetically.

In 1948 Néel proposed the existence of a third type of cooperative magnetic phenomenon called *ferrimagnetism*. Here an apparent ferromagnetism arises from the antiparallel coupling between two non-equivalent magnetic sublattices. The sublattices may contain either different magnetic ions or correspond to identical ions on different crystallographic sites. If the saturation magnetization of each lattice is of simple form then the resultant magnetization versus temperature curve of a ferrimagnetic substance resembles that of a ferromagnetic one, as illustrated in Figure 1c.

#### Orbital and Spin Moments

Magnetic moments are expressed in Bohr magnetons ( $\mu_B$ ); this is the natural unit of magnetism and is equal to the magnetic moment of an electron assumed to be spinning about its axis. It is given by  $eh/4\pi mc$  and has the numerical value  $9.273 \times 10^{-21}$  erg gauss $^{-1}$ ;  $e$  is the charge and  $m$  the mass of an electron;  $h$  is Planck's constant and  $c$  the velocity of light.

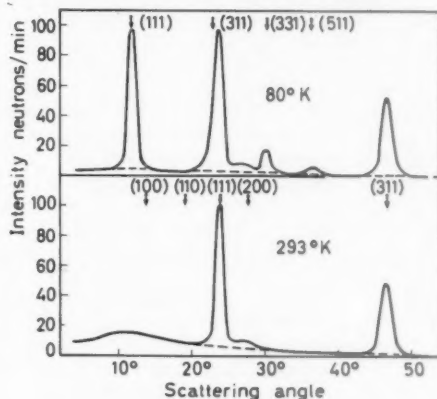


Figure 2. The neutron diffraction patterns of MnO at 80° and 293°K showing extra antiferromagnetic reflections below the Néel temperature<sup>2</sup>

If the magnetization of ferromagnetic and ferrimagnetic compounds is entirely due to the spin motion of unpaired electrons one should expect the moment of each ion to be  $2S\mu_B$  where  $S$  is the total spin angular momentum. If, however, there is a contribution from the orbital motion the ionic

moment is  $gS\mu_B$ , where  $g$  is given by twice the total magnetic moment divided by the spin moment and is greater than two. Effective  $g$ -factors may be determined by microwave resonance absorption. In the compounds to be considered the magnetic

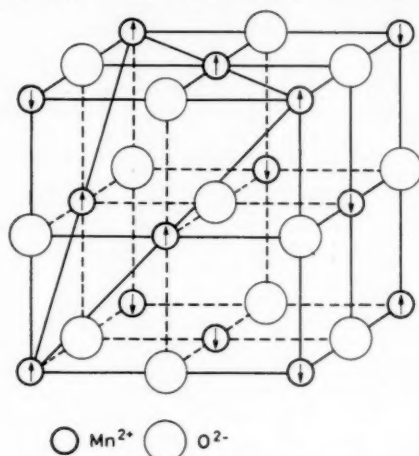


Figure 3. The magnetic structure of MnO below the Néel temperature. A (111) plane of the magnetic unit cell is indicated

moment of the transition metal ions is usually close to the  $2S$  value (i.e.,  $N\mu_B$  for  $N$  unpaired  $3d$  electrons), showing that the orbital contribution is small.

#### Magnetic Measurements

For antiferromagnetism the significant measurement is that of the paramagnetic moment above the Néel temperature. Below the Néel temperature the observed paramagnetic susceptibility is related to the disturbance of the antiparallel arrangement of atomic moments by the applied magnetic field. The susceptibility is therefore a maximum at the Néel temperature. For ferromagnetic and ferrimagnetic substances the significant magnetic property is the absolute or spontaneous magnetization within the Weiss domains at zero temperature and in the absence of an external field. In practice the saturation magnetization  $I_{H,T}$  is measured but the spontaneous magnetization  $I_{0,0}$  may be found by extrapolating the results obtained at different field strengths and different temperatures to  $H = 0$  and  $T = 0$ . The spontaneous magnetization at  $0^\circ\text{K}$  per molecule or formula unit is hereafter called the saturation moment and is given by

$$n_B = \frac{I_{0,0}M}{Nd\mu_B} \text{ Bohr magnetons}$$

where  $M$  is the molecular weight,  $N$  is Avogadro's number and  $d$  the density.

#### Antiferromagnetic Compounds

It is convenient to start the study of cooperative magnetism in oxides and related compounds by considering the antiferromagnetic oxide MnO. In common with the other divalent oxides of the first transition metals, MnO crystallizes in the cubic NaCl-type structure. The  $\text{Mn}^{2+}$  ions form a face-centred cubic lattice so that each ion has twelve nearest neighbours and six next nearest neighbours which are blocked by oxygen ions.

The first definite indication of antiferromagnetism in MnO was the observation of H. BIZETTE, C. F. SQUIRE and B. TSAI<sup>1</sup> in 1938 that the curve of magnetic susceptibility versus temperature had a well developed peak at about  $116^\circ\text{K}$  which fitted the predicted feature of antiferromagnetism proposed previously by Néel<sup>2</sup>. The transition from an ordered antiferromagnetic to disordered paramagnetic structure at the Néel temperature is also indicated by  $\lambda$ -type peaks in the specific heat and thermal expansion. The paramagnetic susceptibility above the Néel temperature obeys the Curie-Weiss law giving an effective moment of  $5.95 \mu_B$  for the  $\text{Mn}^{2+}$  ion compared with the theoretical value of  $5.92 \mu_B$  for a spin of  $5/2$ . (The paramagnetic moment is  $2\sqrt{S(S+1)} \mu_B$ , not  $2S\mu_B$  as for the ferromagnetic moment.)

Direct proof that MnO and the related oxides FeO, CoO and NiO contain an ordered arrangement of antiparallel spin orientations below their Néel temperatures was obtained from neutron diffraction experiments<sup>3</sup>. Neutrons are scattered both by atomic nuclei, giving a similar diffraction pattern as x-rays, and by the magnetic moments of unpaired electrons. Thus, below the Néel temperature extra reflections are present from which it is possible to obtain the probable spin orientations in the lattice. The neutron diffraction pattern of MnO above ( $293^\circ\text{K}$ ) and below ( $80^\circ\text{K}$ ) the Néel temperature is shown in Figure 2. The extra Debye-Scherrer peaks due to magnetic scattering can be indexed on the basis of a magnetic cubic cell of double the dimensions of the chemical cell.

Of the various possible magnetic structures tested by C. G. SHULL and his co-workers<sup>3</sup>, only that illustrated in Figure 3 gave satisfactory agreement between the observed and calculated intensities of the magnetic peaks. The striking feature of this spin lattice structure is that all next-nearest neighbours have antiparallel spin orientations which suggests that coupling between a pair of  $\text{Mn}^{2+}$  ions takes place via an intermediate oxygen ion. The phenomenon of indirect exchange interaction occurring via intermediate non-magnetic ions is common to all types of cooperative magnetism in non-metallic compounds, as will be seen later.

Observations of the magnetic (111) diffraction peak of MnO at intermediate temperatures show that its intensity falls to zero in the neighbourhood of the transition temperature as deduced from specific heat and susceptibility measurements (Figure 4). Similar diffraction data for the oxides FeO, CoO and NiO suggest Néel temperatures of 198°, 271° and 650°K respectively, in good agreement with the values found from specific heat and susceptibility measurements. FeO differs, however, from the other oxides in that the magnetic moments are aligned normal to the 'ferromagnetic' (111) planes instead of along the cube axes. This fact is detected by the absence of the magnetic (111) reflection.

### Superexchange Interaction

The high Néel temperatures of MnO and related oxides show that the coupling between next-nearest neighbour magnetic ions is comparable in strength to that found in ferromagnetic metals, even though

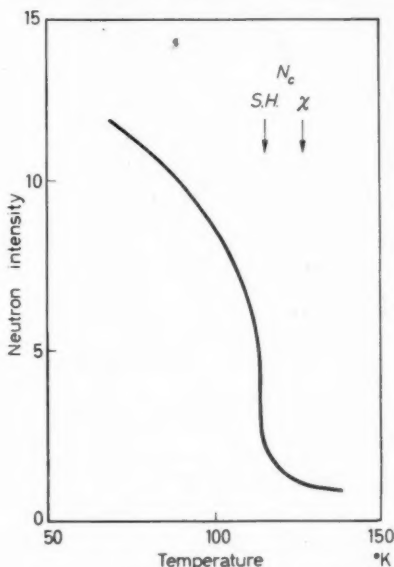


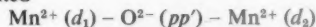
Figure 4. Fall in intensity of the (111) magnetic reflection of MnO in the region of the Néel temperature. Arrows indicate values of Néel temperature deduced from specific heat and susceptibility measurements<sup>3</sup>

in the former case the magnetic ions are separated by non-magnetic oxygen ions.

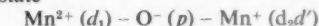
The way in which the electron densities of the magnetic ions can 'overlap' and give rise to a magnetic exchange interaction is interpreted in terms of the theory of *superexchange* interaction proposed

by H. A. KRAMERS<sup>4</sup> in 1934 to account for the magnetic interaction in certain salts in which magnetic ions are separated by large distances, e.g., 5.55 Å in CuSO<sub>4</sub>·5H<sub>2</sub>O ( $N_c = 0.7^\circ\text{K}$ ). According to this theory the electron spins of the cations are linked by excited paramagnetic states of the intermediate anions.

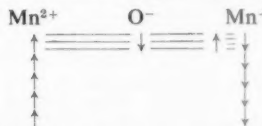
P. W. ANDERSON<sup>5</sup> developed the theory of superexchange interaction and applied it to MnO briefly as follows: In the ground state (lowest energy) a single colinear configuration Mn-O-Mn may be represented



where  $d_1$  and  $d_2$  represent the total (five) unpaired electrons in the 3d orbits of the Mn ions, and  $p$  and  $p'$  represent the two electrons in the bonding 2p orbital of the oxygen ion. An excited state of higher energy is formed if one oxygen electron ( $p'$ ) moves into the 3d orbit of a Mn ion (becoming  $d'$ ). According to the Pauli Principle the spin of the transferred electron will be antiparallel to the resultant spin of the electrons ( $d_2$ ) already present. A mixture of the two states has a lower energy than the original ground state (quantum mechanics) so that the excited state



is stabilized. In this excited state the electron ( $p$ ) remaining on the oxygen ion can couple with the resultant electron spin of the  $\text{Mn}^{2+}$  ion ( $d_1$ ). Finally, since the electrons originally on the oxygen ion had antiparallel spin there will appear to be an indirect *negative* exchange coupling between the spins of the two Mn ions. This may be illustrated:



If this principle is extended to all configurations Mn-O-Mn in MnO the antiferromagnetic structure shown in Figure 3 is formed.

The theory of superexchange interaction correctly predicts the antiferromagnetic properties of many other compounds; e.g., the oxides, sulphides and fluorides of divalent Mn, Fe, Co and Ni, MnSe and MnTe.

If the magnetic ions have less than half filled 3d shells then the above picture of superexchange predicts a *positive* interaction between the ions (parallel spins) since in accordance with a strong Hund's rule effect the transferred electron will enter the 3d orbit with parallel spin. It is a fact that whereas MnTe is antiferromagnetic CrTe, where  $\text{Cr}^{2+}$  is  $3d^4$ , is ferromagnetic. Also MnBi, MnAs and MnSb are ferro-

magnetic ( $\text{Mn}^{3+}$  is  $3d^4$ ). However there are cases where ferromagnetism is predicted yet antiferromagnetism is found; e.g.,  $\text{Cr}_2\text{O}_3$  and  $\text{LaMnO}_3$ , but their special cases will be dealt with later.

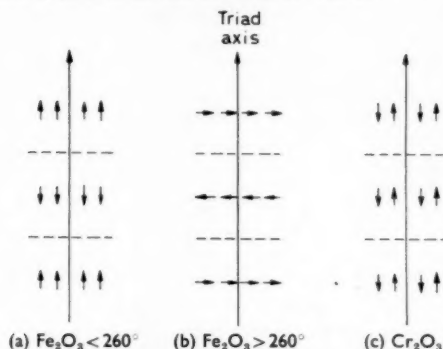
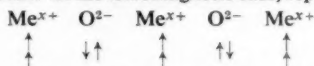


Figure 5. Schematic representation of the direction of spin moments of  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  ions in the cation (111) layers of  $\text{Fe}_2\text{O}_3$  and  $\text{Cr}_2\text{O}_3$  perpendicular to the triad axis. Oxygen ion layers alternate with the cation layers

### Superexchange and Electronic Conduction

An interesting feature of the Anderson superexchange model is that it predicts quite different characteristics of electronic conduction for the antiferromagnetic and ferromagnetic compounds discussed so far. In the ferromagnetic case, represented:



under the influence of an applied electric field, an electron with 'spin up' can travel easily down the line of alternate metal and oxygen ions providing that 'vacancies' occur in the oxygen  $2p$  orbitals, that is, the oxygen ions are in excited paramagnetic states. Since transitions involving spin reversal are energetically less favourable, the conductivity of such a system should decrease with temperature as the ideal lattice at  $0^\circ\text{K}$  becomes progressively disturbed.

In the antiferromagnetic case, however, a similar easy electron motion is not possible in the ideal lattice at  $0^\circ\text{K}$  (see illustration of  $\text{Mn}^{2+}-\text{O}-\text{Mn}^{2+}$  above). At finite temperatures due to thermal vibration, rotation *etc* reversed spins exist and each reversed spin presents the possibility of conduction, so that conduction, although poor, should increase with increased temperature.

It is a striking confirmation of the theory<sup>6</sup> that whereas the antiferromagnetic compounds  $\text{MnO}$ ,  $\text{FeO}$ ,  $\text{MnS}$ ,  $\text{MnTe}$  *etc* are poor conductors with resistivities in the range  $10^3$  to  $10^{10}$  ohm cm and have

negative temperature coefficients of resistance, the ferromagnetic compounds  $\text{MnBi}$ ,  $\text{MnAs}$ ,  $\text{MnSb}$  and  $\text{CrTe}$  have resistivities in the range  $10^{-3}$  to  $10^{-4}$  ohm cm and have positive temperature coefficients.

### The Hematite Structure

Hematite,  $\alpha\text{-Fe}_2\text{O}_3$ , and chromic oxide  $\text{Cr}_2\text{O}_3$  crystallize in a rhombohedral structure in which almost plane layers of oxygen ions, and cations in six-fold coordination, alternate perpendicular to the triad axis. The oxygen ions, to a first approximation, form a hexagonal close-packed structure. Both oxides are antiferromagnetic— $\alpha\text{-Fe}_2\text{O}_3$  also has a very small parasitic ferromagnetic moment of about  $0.1 \mu_B$  per molecule which may arise from a defect of stoichiometry or from domain wall effects, but this will not be discussed—and their magnetic structures have been determined from magnetic studies and directly from neutron diffraction experiments.

In  $\text{Fe}_2\text{O}_3$  each cation (111) layer is spontaneously magnetized to saturation but successive layers are magnetized in opposite directions<sup>3</sup>. The strong negative interactions between layers are explained in terms of superexchange of the type  $\text{Fe}-\text{O}-\text{Fe}$ . In contrast to the compounds discussed so far the interacting configurations are not colinear, but this condition is not explicit in the theory of Anderson. All that is necessary is that the orbitals of the interacting metal ions overlap the two lobes of the intermediate oxygen  $2p$  orbital. The strength of the interaction is a maximum therefore for a colinear configuration, since the overlap is then a maximum (for given  $\text{Me}-\text{O}$  distances), and weakest for an angle of  $90^\circ$ . The strength of the interaction also depends on the inter-ion distances  $\text{Me}-\text{O}$ , so that both configuration angle and  $\text{Me}-\text{O}$  distances must be considered when predicting the predominant interactions in a non-linear structure. For two configurations  $\text{Me}-\text{O}-\text{Me}$  with approximately equal angle the one with the shorter distance(s)  $\text{Me}-\text{O}$  should be the stronger.

In  $\alpha\text{-Fe}_2\text{O}_3$ , the magnetic structure can be explained<sup>7</sup> in terms of two strong superexchange interactions where the configuration angles are  $117^\circ$  and  $133^\circ$  and the  $\text{Me}-\text{O}$  distances are either  $1.97$  or  $2.07 \text{ \AA}$ . Below  $260^\circ\text{K}$  the direction of antiferromagnetism coincides with the triad axis (Figure 5a); above  $260^\circ\text{K}$  the direction is in a plane perpendicular to the triad axis (Figure 5b) but with no specific orientation in the plane.

The magnetic structure of  $\text{Cr}_2\text{O}_3$  (Figure 5c) presents a more difficult problem. According to the original theory of Anderson all superexchange interactions should be positive (leading to ferromagnetism) as  $\text{Cr}^{3+}$  has a less than half filled  $3d$  shell.

Recently Anderson and H. HASEGAWA have stated that the omission of a term in the original perturbation calculations may be significant. To explain the occurrence of antiferromagnetism in  $\text{Cr}_2\text{O}_3$  it is necessary to assume that one interaction  $\text{Cr}-\text{O}-\text{Cr}$ , analogous to the configuration with angle  $117^\circ$  in  $\alpha\text{-Fe}_2\text{O}_3$ , is negative. E. W. GORTER<sup>7</sup> has recently discussed the problem.

A third antiferromagnetic compound having the hematite structure is ilmenite,  $\text{FeTiO}_3$ . In the ideal structure layers of  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  alternate with layers of oxygen ions perpendicular to the triad axis, and antiferromagnetism might be due to either antiparallel orientation of  $\text{Fe}^{2+}$  moments within each iron layer or antiparallel orientation of successive layers. However, it is not certain that a completely ordered arrangement of  $\text{Fe}^{2+}$  and  $\text{Ti}^{4+}$  ions exists in  $\text{FeTiO}_3$  since x-ray diffraction cannot determine the positions of the ions with sufficient accuracy. There is therefore the possibility of antiferromagnetic coupling of the iron layers via  $\text{Fe}^{2+}$  ions in the  $\text{Ti}^{4+}$  layer. No satisfactory explanation has yet been given.

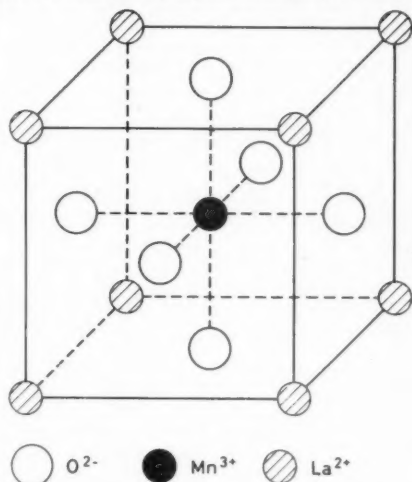


Figure 6. The perovskite structure, e.g.,  $\text{LaMnO}_3$

### The Perovskite Structure

Many compounds of the type  $\text{ABO}_3$  where A is La, Ca, Ba, Sr *etc* and B is Mn, Co, Cr, Ni *etc* crystallize in one or other modification of the cubic perovskite structure (Figure 6) and exhibit antiferromagnetism or ferromagnetism according to composition. Much work has been done on the manganites and these compounds will be considered first.

Historically, G. H. JONKER and J. H. VAN SANTEN<sup>8</sup> in 1947 found that lanthanum manganite, ideally

$\text{LaMnO}_3$ , showed ferromagnetic properties at  $78^\circ\text{K}$  providing the material contained some  $\text{Mn}^{4+}$  ions, formed by preparing the material in a too oxidizing atmosphere. Since  $\text{Mn}^{4+}$  occurs in the compounds  $\text{Me}^{2+}\text{MnO}_3$ , an investigation was made of the magnetic properties of the mixed crystals  $\text{LaMnO}_3\text{--Me}^{2+}\text{MnO}_3$ , i.e.,  $\text{La}_{1-x}\text{Me}_x\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+}\text{O}_3$ , where  $\text{Me}^{2+}$  is Ca, Ba, Sr, Cd *etc*. In a number of experiments also La was replaced by trivalent rare earth metal ions. All systems were found to exhibit ferromagnetism over a certain range of composition, usually with a maximum saturation magnetization and Curie temperature in the range 25 to 40 per cent  $\text{Mn}^{4+}$  ( $0.25 < x < 0.4$ ). Moreover, within this range the observed magnetizations agreed well with the calculated values for spin only contribution of the  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions; *g*-factors close to 2.0 confirmed the lack of orbital contribution.

More recently the  $(\text{La}, \text{Me}^{2+})\text{MnO}_3$  system has been investigated by E. O. WOLLAN and W. C. KOEHLER<sup>9</sup> using neutron and x-ray diffraction. In addition to ferromagnetism the system was shown to exhibit antiferromagnetism corresponding to at least five (probably seven) antiferromagnetic structures. The different structures are related to the relative  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ion content and to the actual cation composition. Pure ferromagnetism is found only in the narrow composition range about  $x \sim 0.35$ , but simultaneous ferromagnetism and antiferromagnetism occurs in the ranges  $0 < x < 0.25$  and  $0.4 < x < 0.5$ . Several types of antiferromagnetic structure are found at  $x=0$  and  $x>0.5$ .

### Ferromagnetic Double-Exchange Interaction

In the mixed-manganite system under discussion three possible exchange interactions are to be considered:  $\text{Mn}^{3+}\text{--Mn}^{3+}$ ,  $\text{Mn}^{3+}\text{--Mn}^{4+}$  and  $\text{Mn}^{4+}\text{--Mn}^{4+}$ . In each of these cases the interactions may occur via the linear configurations  $\text{Mn--O--Mn}$  which correspond exactly with the type of configuration for which Anderson<sup>5</sup> developed the theory of superexchange interaction. However, since  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions have less than half filled 3d shells, one should expect according to superexchange theory positive interactions (and hence ferromagnetism) to occur in all compositions, which is in sharp contrast to the observed magnetic properties. For this, and other reasons<sup>10</sup>, it is concluded that superexchange is completely inadequate for the magnetic perovskite systems.

An explanation of the positive interaction or real ferromagnetism in the perovskite manganites was proposed in 1951 by C. ZENER<sup>11</sup>. If a disordered arrangement of ferromagnetically coupled  $\text{Mn}^{3+}$  and

$Mn^{4+}$  ions occur in the perovskite lattice the state  $Mn^{3+}-O-Mn^{4+}$  is degenerate with the state  $Mn^{4+}-O-Mn^{3+}$ , so that a strong resonance will take place through the intermediate oxygen ion.

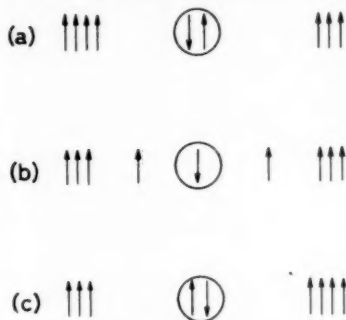


Figure 7. Schematic illustration of double exchange interaction between the degenerate states  $Mn^{3+}-O-Mn^{4+}$  (a) and  $Mn^{4+}-O-Mn^{3+}$  (c) via the transition state (b)

The mechanism of the electron exchange interaction may be visualized in the following way: A  $d$  electron from an  $Mn^{3+}$  ion is excited into the overlapping oxygen  $2p$  orbital while simultaneously the oxygen electron of parallel spin is excited to the  $Mn^{4+}$  ion. In this way the two manganese ions exchange identity (Figure 7). An attractive feature of this double exchange mechanism is that electron exchange occurs without a change of spin orientation, so that relatively high electrical conductivity is expected in the ferromagnetic region which is in excellent agreement with observation. This is illustrated in Figure 8 for the system  $(La, Sr)MnO_3$ .

Although double exchange has achieved success in explaining the ferromagnetic properties of certain systems it does not appear to be universally correct. Thus, while similar magnetic and electrical properties are found with the corresponding compounds containing  $Co^{3+}-Co^{4+}$ , those with  $Cr^{3+}-Cr^{4+}$  and  $Fe^{3+}-Fe^{4+}$  are good conductors but antiferromagnetic<sup>12</sup>. Also a recent theoretical examination of the double exchange interaction<sup>13</sup> concludes that this interaction should be lost above the Curie temperature, but it is found that the magnetic perovskites obey the Curie-Weiss law which means that exchange interactions are still operative.

### Semicovalent Exchange

A remarkable phenomenological explanation of the magnetic structure, the crystallographic structure, the electrical resistivity and the ferromagnetic Curie temperature of the perovskite-type manganites  $(La, Me^{2+})MnO_3$  as a function of the  $Mn^{3+}/Mn^{4+}$

content has been presented by J. B. GOODENOUGH<sup>10</sup>. The new theory takes into account the possibility of the participation of empty cation  $4s$  or  $4p$  orbitals in the electron energy system. This had been ignored in previous theories on the assumption that since the empty orbitals have much higher energies than the cation  $3d$  or anion  $2p$  orbitals they could have little effect on the state of the electrons in the essentially ionic system.

Goodenough, however, postulated that as a result of strong perturbations of neighbouring atoms on one another, the empty atomic orbitals may become equivalent to lattice orbitals and that these may be nearly degenerate with the atomic  $3d$  orbitals. If then the most stable of the empty orbitals strongly overlap the full  $2p$  orbitals of the neighbouring oxygen ions, an oxygen electron may spend part of its time in what is effectively an extended cation  $d$  orbital; moreover, it may do so without a change of spin orientation and without completely losing its identity as an oxygen electron.

In contrast to normal covalent bonding, if the cation has an oriented magnetic moment the two oxygen electrons do not have a equal probability

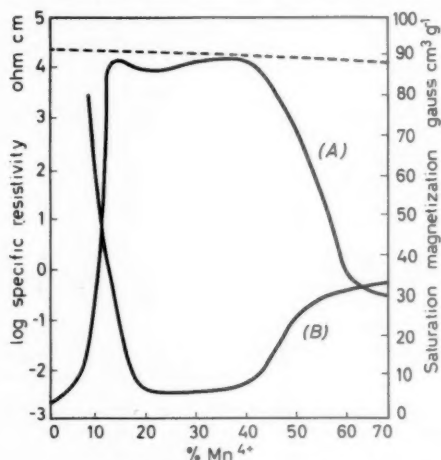


Figure 8. Variation of saturation magnetization at 20.4°K (curve A) and specific resistivity (curve B) of  $(La, Sr)MnO_3$  as a function of the  $Mn^{4+}$  content. The dashed line represents calculated spin-only values of saturation magnetization<sup>6,12</sup>

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stabilization of antiferromagnetic exchange coupling in the perovskite-type manganites can be explained. Because a single electron predominates in the bond it is termed a *semicovalent bond*; the resulting magnetic exchange interaction, which is illustrated in Figure 9, is therefore termed *semicovalent exchange*.

The theory of semicovalent exchange has been criticized in that it is essentially phenomenological and cannot predict the magnetic properties of other ionic systems, but its success in accounting for the



Figure 9. Illustration of semicovalent exchange in the collinear system  $Me-O-Me$

structural and magnetic properties of the perovskite-type manganites is remarkable. For this system Goodenough uses the Zener double exchange model to account for the region of positive interaction between  $Mn^{3+}$  and  $Mn^{4+}$  ions, and in an appendix to the main paper<sup>10</sup> he presents a statistical explanation for the occurrence of peak ferromagnetism at the composition containing 30 per cent  $Mn^{4+}$ , whereas on first sight one would expect the peak to occur at equal  $Mn^{3+}$  and  $Mn^{4+}$  content.

### Perovskite-Type System $(La, Sr)CoO_3$

It has already been pointed out that the theories of magnetic exchange so far discussed are not universal in their ability to explain the properties of apparently similar systems, and in this respect it is interesting to mention briefly the very recent interpretation by Goodenough<sup>14</sup> of the anomalous magnetic properties of the perovskite-type mixed crystals  $(La, Sr)CoO_3$ . Both antiferromagnetic and ferromagnetic structures occur according to composition but the effective paramagnetic moments and the saturation moments are considerably less than the values predicted from spin-only contribution of  $Co^{3+}$  and  $Co^{4+}$  ions. The system also possesses other structural and magnetic anomalies which cannot be satisfactorily interpreted in terms of forementioned theories.

Goodenough has considered in detail the effect of splitting of the atomic 3d energy levels by the crystalline fields encountered in the perovskite-type lattice, and concludes that a  $Co^{3+}$  ion in an octahedral site has a low spin and a high spin state of

comparable energy while the  $Co^{4+}$  ion exists in this structure only in a low spin state. It is further postulated that ordering of low spin and high spin states occurs in two sublattices, each consisting of sets of (111) planes, such that each sublattice contains only one spin state. The experimental results can be explained if the magnetic interaction between high spin  $Co^{3+}$  ions is antiferromagnetic while the interaction between low spin  $Co^{4+}$  and high spin  $Co^{3+}$  ions is ferromagnetic. A feature of this model is that the ferromagnetic region in the system can be explained without invoking Zener's double exchange mechanism.

### Conclusion

In this paper the occurrence in oxide structures of antiferromagnetism, through indirect negative magnetic exchange, and of ferromagnetism, through indirect positive magnetic exchange, has been considered in the light of experimental evidence. It has not been possible to cover the whole of the field, but the important systems and concepts have been mentioned. In Part II of the series the occurrence of ferromagnetic properties through what is essentially an antiferromagnetic exchange process is described for several oxide systems. The compounds to be considered include the well known ferrimagnetic spinels (ferrites).

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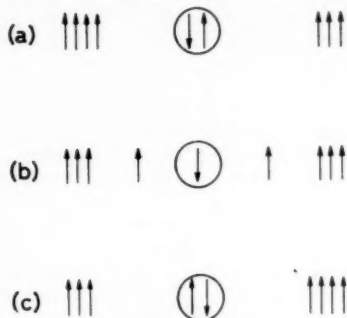


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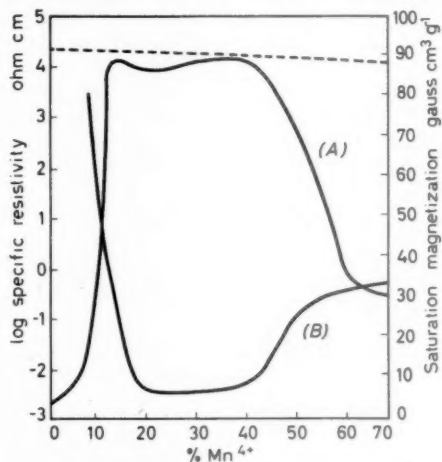


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# THE USE OF RADIOACTIVE ISOTOPES

## Part II—Metallurgical Applications

C. G. CLAYTON

*Isotope Division, Atomic Energy Research Establishment, Harwell*

In the first part, a brief survey of the production and properties of radioisotopes, the best methods available for detecting radiations and the accuracy of these methods was made\*. These general principles were then applied to problems in the engineering industry and the present article will now proceed to consider some of the many metallurgical applications.

THE FIRST part of this paper, which dealt with the engineering applications of radioisotopes, included a review of the general methods which are used at present for preparing these isotopes. The common methods of detecting alpha, beta and gamma radiations were outlined. Geiger or scintillation counters are used to detect and measure beta and gamma radiations and, although these can also be adapted for alpha particles, it is more usual to detect and measure alpha particles by their effect on photographic emulsion. Ionization chambers will detect alpha, beta and gamma particles but they are generally used to determine the total ionization current produced. An estimate of the accuracy with which radioactive disintegrations can be determined was given in the first part.

The second part will now proceed to consider the application of radioactive isotopes in metallurgy: firstly the application in industry and secondly the application in research.

### The Blast Furnace

Radioisotopes have been used to study many dynamical characteristics of the smelting process in the blast furnace. L. BOGDANDY and R. SCHMOLKE<sup>1</sup> have carried out experiments to determine the rate of disintegration of an agglomerate inside a blast furnace and they concluded that the proportion of dust thrown out at the furnace mouth was 4.5 per cent when the agglomerate was in the form of sintered briquettes and 13.5 per cent when in the form of cold compacted briquettes.

A. KOHN<sup>2</sup> has also made a number of tracer experiments in blast furnaces. Using  $\text{Au}^{198}$ , which dissolved in the pig iron, and  $\text{La}^{140}$ , which was absorbed into the slag, he found that the lumps of

ore took less than four hours to be converted into pig iron and slag whilst the coke took about eight hours to descend through the furnace. Information was obtained from samples of pig iron and slag taken at various intervals after the introduction of the radiotracer.

By introducing  $\text{P}^{32}$  through the tuyeres of a blast furnace, W. LOORZ and H. WEBER<sup>3,4</sup> were able to obtain information on the general turbulence pattern inside the furnace. They showed that the slag at the surface of the melt was only slightly disturbed, probably due to its high viscosity, whereas the iron in the hearth was significantly agitated due to convection currents. From samples of metal obtained from tapping the furnace it was shown that in less than two hours after the introduction into the melt, the radioisotope was distributed throughout 70 tons of pig iron contained in the hearth. E. EICKWORTH, *et al.*<sup>5</sup> also used  $\text{P}^{32}$  to measure the mixing efficiency of iron in a 850 ton mixer. The phosphorous, as iron phosphate, was pre-mixed by dissolving in a 40 ton melt and then, on different occasions, poured into the mixer when it was full, half full and quarter full. The mixing efficiency was determined from samples of the metal drawn off from the mixer, and the mixing efficiency was found to be satisfactory. This was attributed to strong convection currents in the liquid metal.

The general application of radioisotopes to the measurement of mixing efficiencies is an important one. In some cases where one material is added in small quantities to a large bulk of another, chemical analysis can be used, but it is usually much more tedious than the introduction of radiotracers. If a unique solution to the flow pattern, or dynamic characteristics, of a system is required, then the use of radioisotopes is likely to be the only way in which this can be done.

\*CLAYTON, C. G., *Research, Lond.* (1959) 12, 148

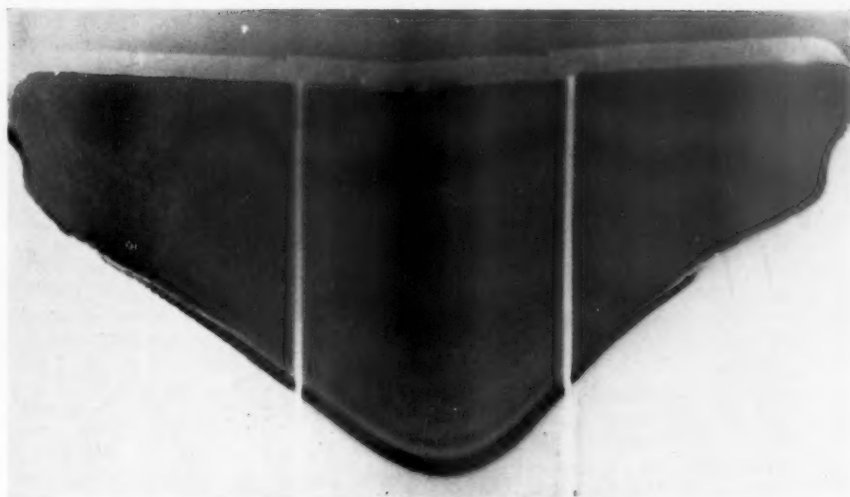


Figure 1. Autoradiograph showing solidification boundary of continuously cast aluminium (by courtesy of the Institute of Metals)

### Wear of Blast Furnace Lining

Important information has been obtained on the rate of wear of refractory furnace linings by the use of radioisotopes. Using sources up to 150 mc inserted in one of the refractory bricks, the rate of wear was determined either

(i) by using a detector placed adjacent to the source and determining the decrease in radiation level during the operation of the furnace, or

(ii) by measuring the radioactivity of samples removed from the furnace during tapping.

Using the method of external measurement it is possible to investigate simultaneously the rate of wear at different levels, and this was the method adopted by the earliest British workers in this field. More recently, however, P. L. GRUZIN and S. N. ZEMSKY<sup>8</sup> have made similar investigations using isotopes with different gamma ray energies inserted at different levels in the furnace. They obtained samples from the melt, and after determining the radiation energy of the samples, it was possible to say in which part of the furnace wear was occurring. In these experiments  $P^{32}$  and  $Ir^{192}$ , which have relatively short half lives, were incorporated into the walls in the upper part of the hearth, where wear is most rapid, whereas in the lower part of the hearth, which has a lower rate of wear,  $Ag^{110}$ ,  $Sr^{90}$ , and  $Co^{60}$  were used.

From experiments of this type it has been possible to establish a common pattern of wear for different parts of a blast furnace but the actual degree of

wear depends on such things as the refractories used, the type of iron produced and the particular type of cooling arrangement adopted.

### Refining and Casting

A number of workers have studied various aspects of the refining and casting process. W. KOCH and K. FINK<sup>7</sup> investigated the conditions governing the absorption of sulphur from the atmosphere by the metal in an open hearth furnace. They showed that between 10 and 20 per cent of the sulphur content of the gas passed into the metal during melting, but only one per cent of the fuel was absorbed by the metal bath. Other workers<sup>8,9</sup> have used  $S^{35}$  to determine the factors controlling the removal of sulphur from the melt during refining. These workers established a value for the partition coefficient of the sulphur between bath and slag, and between slag and gases. They demonstrated that the rate at which sulphur is removed depends on the basicity of the slag and the agitation of the bath.

$Fe^{55}$  and  $Fe^{59}$  have been used to determine the melting rate of scrap iron after its introduction into the furnace<sup>10</sup> while  $P^{32}$  and  $Co^{60}$  have both been used to ascertain the degree of turbulence in the liquid metal<sup>11,12</sup>. It was shown that complete mixing of the isotope was accomplished within one hour of its introduction into a 350 ton furnace.

In an excellent review of the subject, Kohn<sup>13</sup> has reported several investigations to discover the origin of inclusions in ball bearing steels.  $Ca^{45}$  was

used by incorporating it in refractories at various positions in the furnace and it is generally concluded that the major source of inclusion is from the erosion of the pouring ladle. It was discovered that

since it not only removes all question of radiation hazard but it also avoids the contamination of a large bulk of material when only small samples might be required.

To remove fission products which usually have a high capture cross section for thermal neutrons, reactor fuel elements have to be processed at regular intervals. J. E. ANTILL *et al.*<sup>15</sup> have considered the possibility of using zone melting as an alternative to chemical separation and they describe an interesting application of natural radioactivity to measure the efficiency of the zone melting process.

Metallic solutions of cobalt in uranium and ruthenium in uranium were studied using the gamma emitting isotopes  $\text{Co}^{60}$  and  $\text{Ru}^{103}$ . After zone melting, the bar was cut into sections each one millimetre thick, and assayed for radioactivity. Since uranium is one of the densest elements it was thought that differences in specific gravity might be used to increase the zone separation. The results obtained for uranium containing 800 p.p.m. ruthenium when the zone was passed upwards and downwards at 0.25 in. per hour prove that even for soluble impurities at low concentrations, density effects can be used with advantage. Uranium bars, irradiated in a neutron flux of  $2.5 \times 10^{10}$  neutrons/cm<sup>2</sup>/sec for five hours and cooled for eight days have been zone melted, passing the zone upwards at a speed of three inches per day. The result of this purification, measured by the total gamma activity, filtered through 0.024 in. of lead, is shown in Figure 2.

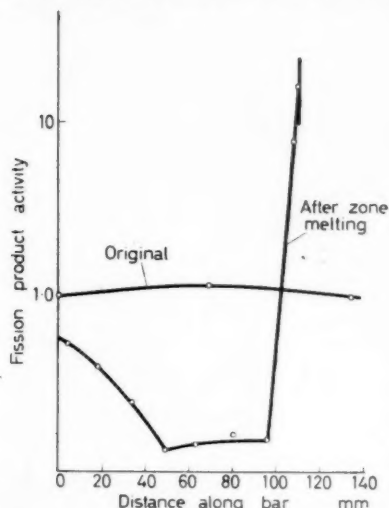


Figure 2. Irradiated uranium bar zone melted with a zone speed of three inches per hour

this could be minimized if bricks with a high alumina content were used.

J. L. PUTMAN<sup>14</sup> has employed two methods to determine the solidification boundary of continuously cast aluminium. In the first method  $\text{Au}^{198}$  was pre-mixed with a small quantity of molten aluminium and then added to the stream feeding the ingot mould. Very rapid diffusion took place, thus outlining the profile of the solidification boundary of the billet. An autoradiograph of a section of the billet is shown in Figure 1. In the second method inactive gold was introduced and the sections from the ingot irradiated in a nuclear reactor. After removal the induced activity in the aluminium, which has a short half life (2.27 min), was allowed to decay to zero and autographs were made from the  $\text{Au}^{198}$ , as before. Gold, which has a high excitation cross section for thermal neutrons is particularly favourable for an experiment of this type. The main advantage of this approach is that it avoids the necessity of introducing radiotracers into the foundry, and from this point of view demonstrates an important principle in the application of radioisotopes. Not all tracer investigations can be attacked in this way, however, but it is a method which should always be borne in mind

### Measurement of Impurity Content

One of the applications in research has been the determination of small amounts of impurity present. It is well known that the presence in metals of certain elements, even in concentrations as low as one part in  $10^6$ , may considerably modify their electrical and physical properties. With this small degree of impurity classical methods of analysis are generally inapplicable, but radioactive techniques can often be used.

The most commonly used method is that known as radioactivation analysis. The basis of this method is that the element to be investigated is made radioactive by irradiation in a reactor, and the induced radioactivity is then used as a measure of the mass of the element originally present. Because of the extremely high sensitivity of radiation measuring instruments, and because of the specific characteristics of individual isotopes, such as half life, and type and energy of the emitted radiation, radioactivation analysis has proved to be extremely useful.

The least concentration of an impurity which can be detected is inversely proportional to its cross section, and some elements with particularly high cross sections can be detected in concentrations as low as one part in  $10^{10}$ . The case of iridium in steel is a particular example. Iridium has an excitation cross section of 370 barns whilst iron has cross sections of only 0.128 and 0.0028 barns for production of  $\text{Fe}^{55}$  and  $\text{Fe}^{59}$ . The gamma rays emitted by iridium have an energy of 0.3 to 0.5 MeV whilst those from  $\text{Fe}^{59}$  are greater than 1 MeV. The gamma ray spectrometer has no difficulty in differentiating these energies and measuring concentrations of iridium as low as  $10^{-10}$  per gram.

Once the nature of the impurity has been determined, a quantitative estimate of the concentration can be obtained by comparing the induced radioactivity in the specimen against that of a sample of the impurity irradiated at the same time. Using this method, calcium, which is almost impossible to measure by conventional techniques in the range of a few parts per million, has been detected at this concentration as a metallic impurity<sup>16</sup>.

In the field of semiconductors, where purity is so important, the arsenic content and the segregation constant of nickel in germanium, and the arsenic and copper content of silicon have been determined<sup>17</sup> to one part in  $10^{10}$ . Oxygen content has also been determined<sup>18</sup> utilizing the  $(n,\alpha,T)$  reaction on oxygen to give  $\text{F}^{18}$ ; the sensitivity of this method is about 0.1 per cent.

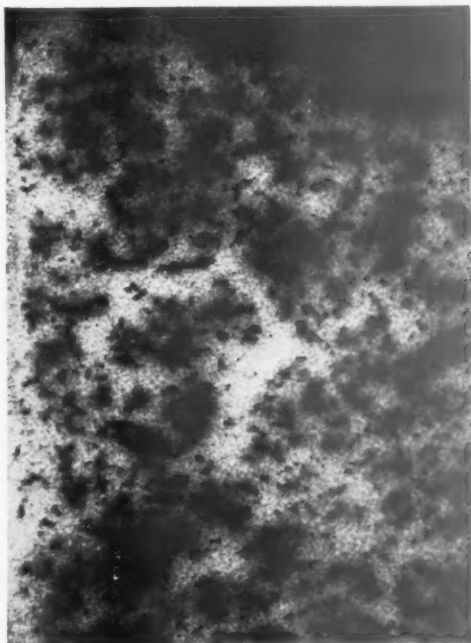
### Diffusion Studies

The rates of diffusion of metals in metals are of great theoretical interest at the present time as they provide information on the structure of alloys, the movement of atoms within metal crystals and on the extent and importance of lattice defects.

Though the diffusion of one metal in a different metal can be determined by orthodox chemical methods, the diffusion of a metal within the same metal can only be studied by radioactive techniques. Following the pioneer measurements in lead by G. HEVESY<sup>19-21</sup> using the naturally occurring radioisotope Th B, the self-diffusion coefficients of most metals that have suitable stable isotopes have been



(a)



(b)

Figure 3. Porosity in a magnesium alloy casting—(a) micrograph; (b) autoradiograph

measured. This early work, and much that followed later, was devoted solely to measurements of overall volume diffusion in a specified direction inside the metal. From work over the past few years, however, it has been revealed that diffusion is a complex

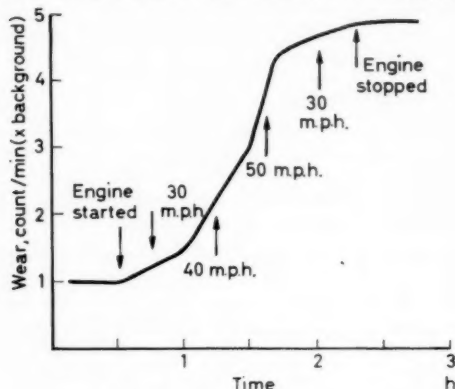


Figure 4. Effect of engine speed on a piston ring wear from measurements of increasing radioactive content of lubricating oil using a radioactive piston ring<sup>28</sup>

process, and diffusion rates vary considerably according to whether the diffusion is a volume effect within the metal grains, or whether it occurs along the grain boundaries. It is known that displacement of atoms can occur only if they have sufficient activation energies and it is known that along the grain boundaries there are smaller free energies, so that the forces opposing the motion of the atoms are reduced, and they can move freely in these regions.

A striking example of the advantage of using radioisotopes in volume diffusion studies is provided by measurements of the diffusion of antimony in silver single crystals<sup>22</sup>. Using ordinary antimony, previous measurements had given an anomalously low value of  $0.16 \times 10^{-5}$  cm<sup>2</sup>/sec for  $D$ , the diffusion coefficient, whereas when Sb<sup>124</sup> was used in sufficiently low concentration, to avoid the effect of concentration on the diffusion coefficient, a value for  $D$  of 0.29 cm<sup>2</sup>/sec was obtained, which is in close agreement with the calculated value.

### Segregation and Surface Defects

The distribution of phases in alloys may be investigated by the autoradiography of active specimens. The location of any constituent can be shown either by adding a radioisotope when preparing the alloy or by irradiating the specimen in a nuclear reactor. Large numbers of metal alloys have been studied

from this point of view, but only two examples will be given. Working with small ingots of very pure iron containing traces of copper, chromium, manganese, tungsten and molybdenum, C. de BEAULIEU and Kohn<sup>23</sup> have shown that these elements do not segregate in the absence of carbon, but do segregate when carbon is present. From these results the authors concluded that dendritic segregation in steels depends mainly on the temperature difference between the start and end of the solidification, since carbon is one of the elements which has the greatest effect on this difference.

In a similar study on nickel, S. T. KISHKIN and S. Z. BOKSTEIN<sup>24</sup> showed that small iron and tungsten impurities are distributed mainly within the dendrites, whereas sulphur, zirconium and tin are concentrated in the inter-dendritic areas. After annealing at a high temperature, some homogenization of the dendritic structure was observed.

An interesting study of surface defects, porosity defects in magnesium alloys, has been reported<sup>25</sup>. This type of defect occurs during the casting process and a typical micrograph of a surface containing pores is shown in Figure 3a. In these experiments Pd<sup>109</sup>, incorporated into a benzene complex, was dissolved in oil, and the specimen immersed in an oil bath. On removal from the bath the surface was cleaned of oil and an autoradiograph taken. The result is seen in Figure 3b where it can be observed that the blackened regions of the autoradiograph match nearly all the regions of porosity visible on the micrograph. With this technique it was possible to detect pores extending from a surface area of  $1.5 \times 10^{-5}$  sq./cm and within 0.4 mm of the surface.

### Friction and Wear

The rate at which metal is removed from a surface as a result of frictional wear is often extremely small and is therefore very difficult to examine quantitatively by ordinary methods. The very high sensitivity of radioactive techniques, and in particular of autoradiography, has enabled vast strides to be made in this field. Engines, machine tools, dies and lubricants have all been studied, and a new attack has been made on the basic process responsible for friction.

The usual technique is to activate one of the parts to be subjected to friction by irradiation in a nuclear reactor. After the friction test the distribution of metal transferred to the slider is examined by autoradiography. It is a simple matter in an experiment of this type to examine the effect of different lubricants on rate of wear and one of the important features of the isotope method is that detailed studies of this kind can be done in a very short time.

Following the earliest experiments using radioisotopes, it was suggested<sup>26,27</sup> that friction and wear may be attributed to the formation of very small welds between the two surfaces in contact, the frictional force being due to the effort required to break these local welds. Later work<sup>28</sup> has shown that this is only part of the process. Initially the rate of transfer of material increases with time until it attains a constant value, though the wear debris then increases as a function of the duration of the experiment. M. KERRIDGE<sup>28</sup> found that for steel sliding on steel the wear debris consisted of iron oxide, and concluded that wear occurs in three stages:

- (i) Material is removed from one surface to the other;
- (ii) The deposited metal is then oxidized; and
- (iii) The particles of oxide formed on the surface are then torn away to form the wear debris.

The wear of dies and cutting tools have been investigated by a number of workers using radioactive techniques. Many workers<sup>29,30</sup> have investigated die wear and have demonstrated, using information obtained mainly from autoradiographic studies, how the die profile could be modified to reduce wear. It has also been shown<sup>31-33</sup> how useful the radioactive technique can be in measuring the wear in cutting tools. It was shown, for instance, that 90 per cent of the fragments

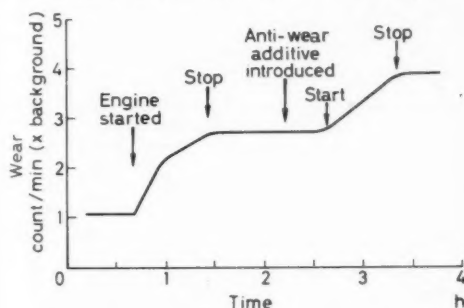


Figure 5. Rate of wear of a piston ring in an internal combustion engine, starting from cold and after introducing an anti-wear additive<sup>28</sup>

removed from a tool during a turning process remained on the turnings, and only a small fraction of the detached particles appeared in the cutting fluid. The same workers have also investigated the effects of different cutting fluids on wear.

The study of wear in internal combustion engines using radioactive isotopes has recently been popularly reported. Following the early work by P. L. PINOTTI *et al.*<sup>34</sup> the subject has received considerable

attention. Of the later work, B. D. GRUZIN<sup>35</sup> has investigated the wear occurring during the running in of aeroplane engines. He used an electrolytic deposit of Zn<sup>65</sup> and, by measuring the increasing radioactivity in the oil circulating system, he obtained information on the influence of load, oil temperature, cylinder head temperature, and finish of the cylinder.

In a recent paper J. H. DETERDING and J. R. B. CALOW<sup>36</sup> have described a method of incorporating a scintillation counter in the oil circulating system of a normal motor car, so enabling measurements of engine wear to be made during normal running conditions on the road. It is generally believed that wear rate increases with engine speed and this has been confirmed by these workers who give a quantitative result for particular conditions of test. Figure 4 shows how, during a certain road test, the rate of piston wear increased at speeds up to 50 m.p.h. and then decreased as the engine speed was reduced. Anti-wear additives were also investigated by the same method and Figure 5 shows how the rate of wear decreased following the introduction of an additive into the oil circulating system.

### Some Comments

Although in this paper, and in Part I, it has only been possible to mention a few of the applications of isotopes in metallurgy and the allied branches of engineering, it will be clear that radioactive isotopes have enabled complete, or more complete, solutions to be derived for very many diverse problems which might otherwise have remained unsolved.

There are of course limitations to the isotope method. There are fundamental processes involving radiation interactions which are not yet fully understood, or completely developed. There are radiation detectors which are inadequate to give the desired stability, and in addition the introduction of radioactive material must be completely controlled so that there is no radiation hazard.

These and other limitations are continuously being reviewed by scientists working on isotope applications. New developments are taking place and it is clear that these techniques will be increasingly applied in new spheres to the general benefit of scientific knowledge and industrial control.

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## 1959 Essay Competition for Schools and Technical Colleges

This year TECHNOLOGY has joined RESEARCH in sponsoring the Competition and extending its scope to include pupils from technical colleges and secondary modern schools. The essays will be judged for content, clarity of presentation and style but account will also be taken, particularly in Section I, of the type of course the entrant is following. Prizes of £15 will be awarded for the best entry and £10 for the next best entry in Sections I and II; prizes to the same value will also be presented to the school or college library of the prizewinners. In Section III there will be a first prize of £30 and a second prize of £20. In each case the prizes may take the form of books or instruments.

*Entries will be accepted after June 1st, 1959 and the final closing date is July 31st, 1959. Please write for full details to The Editor, RESEARCH, 4 and 5 Bell Yard, London, W.C.2.*

### Section I

A report, about 800 words long, on any piece of practical work or project in biology, chemistry or physics written by a school student whose *sixteenth birthday falls on or after June 1st, 1959.*

### Section II

A report about 1000 to 1500 words in length, on any piece of practical work or project in biology, chemistry or physics written by a school student *over the age of sixteen on June 1st, 1959.*

### Section III

A critical essay of about 1000 to 1500 words on which of the 'new' metals promises to be most useful in technology. This section is open to any student attending a technical college who is *under the age of twenty-one on June 1st, 1959.*

# DYEING OF SYNTHETIC FIBRES

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The development of a whole range of synthetic fibres which, unlike viscose and cellulose acetate, are not based on natural products, has provided a host of new dyeing problems. These fibres can at present be dyed with two types of products: ionic dyestuffs which form ionic links with the polymers and 'disperse acetate' dyestuffs.

IN a recent article I. D. RATTEE reviewed<sup>1</sup> the development of synthetic dyestuffs over the last sixty years and discussed their application particularly to the 'traditional' fibres with which the textile industry was concerned prior to about 1930. Since that date, and more particularly in the last fifteen years, there has been added to the natural and regenerated fibres a wide range of new fibres distinguished by the fact that they, like the dyestuffs used to colour them, are the products solely of chemical synthesis, having no natural origins as can be detected in the earlier 'man-made' fibres such as the viscose and cellulose acetate rayons.

The background to the development of these truly synthetic fibres has been discussed from the viewpoint of the polymer chemist by J. C. WARD<sup>2</sup> and it is the purpose of the present article to describe the new problems which these synthetic fibres have brought to the dyeing and dyestuff manufacturing industries and to show how they have been tackled.

## Properties of Synthetic Fibres

Synthetic fibres are characterized by certain features which to a large extent govern both the type of dyestuffs which can be successfully applied to them and the methods of application which have to be adopted. Thus in practically all cases the fibres are chemically simple compared with, say, wool or silk and so the active sites to which dyestuff molecules can bond are limited in range. This in turn tends to limit the number of classes of dyestuffs which can be used on any one fibre.

A further consequence of their simple structure, and one which accounts also for the excellent mechanical properties of many of the fibres, is that the molecular chains tend to form compact structures not easily penetrated by dyestuff molecules. In fact, in regions of the fibre where molecular chain orientation is of such an order that crystallites occur, penetration may be impossible.

## Selection of Dyestuffs

These considerations must clearly influence the selection of dyestuffs and as a result the vat dyestuffs, for instance, which on cellulosic fibres achieve outstanding fastness by reason of their molecular size and configuration, find little application in the colouring of synthetic fibres. Similarly direct dyes which bond readily to the cellulosic chains of cotton and viscose are unable to form similar attachments to fibres of different molecular configuration.

It has been found that only two types of dyestuffs are of interest; those which rely for their affinity on the formation of strong salt linkages within the fibre, such as the anionic 'acid' dyestuffs and cationic 'basic' dyestuffs, and the class of dye which has been developed solely for application to man-made fibres, the 'disperse acetate' dyestuffs. A small number of azoic combinations of bases and coupling components must also be included with the disperse acetate dyestuffs.

## Disperse Dyestuffs

Whilst the disperse dyestuffs were originally developed specifically for the coloration of cellulose acetate rayon they are, as a class, used for dyeing every type of synthetic fibre. Principally they consist of simple anthraquinone and azoic compounds characterized by relatively small molecular size and by the absence of ionizable solubilizing groups in their structures. They therefore have low solubilities in water at normal dyeing temperatures and are applied to the fibres from aqueous dispersions maintained by anionic surface active agents.

Nevertheless, it has been shown<sup>3,4</sup> that transference of dye molecules from the dispersion to the fibre takes place through a solution phase, the dispersion serving as a reservoir to maintain a saturated aqueous solution of the dye at the fibre surfaces. The same workers have also shown that

a constant partition exists between the dyestuff on the fibre and the dyestuff in solution in the dyebath and that this partition is maintained up to saturation of the fibre. This is illustrated by M. J. SCHULER and

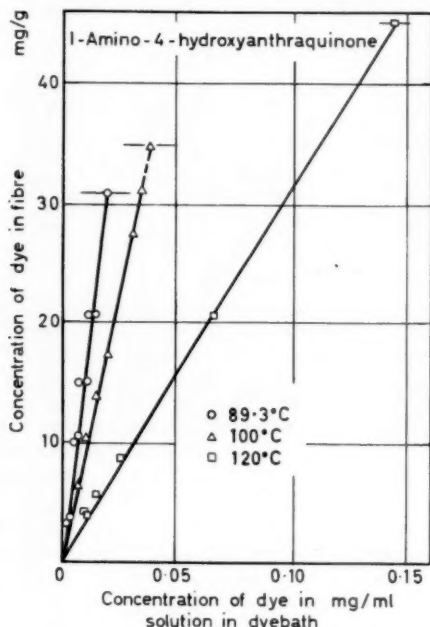


Figure 1. Variation with temperature of the saturation uptake for polyethylene terephthalate

W. R. REMINGTON's results for polyethylene terephthalate, shown in Figure 1, where the variation with temperature of the saturation uptake is evidence of the penetration of dyestuff molecules into the more oriented regions of the fibre at the higher temperatures. The conclusion reached is that the mechanism of dyeing can best be described as solution in the fibre, but figures quoted by T. G. MAJURY<sup>5</sup> for the heat of association of dyestuff and fibre show that the solution is not ideal and that specific bonding must be occurring between dyestuff molecules and the fibre molecular chains.

No one type of bonding force can be postulated to account for the affinity of all disperse dyestuffs for synthetic fibres and there is little doubt that in fact a variety of polar and short range 'dispersion' forces operate in different cases. The existence of 'hydrogen bridges' in model dye-fibre systems has been shown<sup>6</sup> by measurements of refractive index on dyestuffs dissolved in mixtures of water and simple organic solvents corresponding to various fibre structures. Such bonds might operate, for

instance as shown in Figure 2, for two typical disperse dyestuffs applied to polyethylene terephthalate.

Indirect evidence of the importance of polar forces, as might be expected to operate in the case of the molecule in Figure 2b, has been provided by O. GLENZ<sup>7</sup> who compared diffusion rates of dyestuffs exhibiting differing degrees of polarity in basically similar structures. The diffusion rate is dependent upon the degree of bonding to specific sites, those dyestuffs which bond most strongly being the ones which diffuse least readily into the centre of the fibre. Glenz showed that the diffusion rate decreased with increasing polar moment of the dyestuff molecules.

The fact that disperse dyestuffs have only very limited saturation uptake on the polyacrylonitrile fibres, such as 'Orlon', suggests that short range attraction between the aromatic rings of the dyestuff molecules and those of, for instance, polyethylene terephthalate is also responsible for a part of the affinity which the dyestuffs display for such fibres. Support for this view comes from the fact that polyethylene terephthalate fibres are very readily

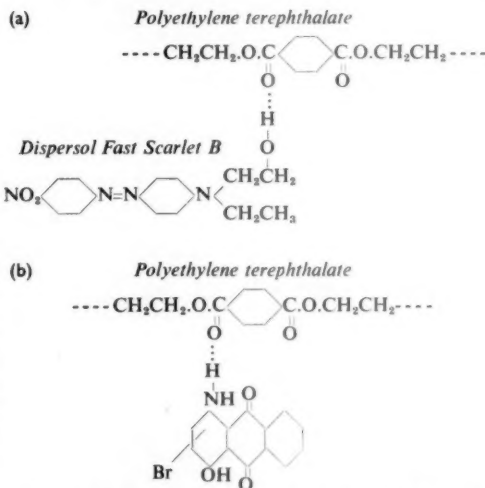


Figure 2. Two typical disperse dyestuffs applied to polyethylene terephthalate—(a) Dispersol Fast Scarlet B (I.C.I. Ltd.) and (b) monobromo-1-amino-4-hydroxyanthraquinone

penetrated by non-polar compounds such as diphenyl which are employed as dyebath additives to increase the rate of uptake of disperse dyestuffs. Known as 'carriers', these compounds by reason of their ease of penetration into the fibre are capable of swelling the fibre and increasing its water uptake,

thereby rendering the internal fibre structure more accessible to the disperse dyestuff molecules. Other compounds which operate in this manner are dichlorobenzene, orthophenyl phenol and benzoic acid, all of which Schuler<sup>8</sup> has shown are equally effective in promoting dye uptake provided they are absorbed by the fibres in equimolecular proportions.

An alternative method of increasing the rate of dyeing and saturation uptake of these synthetic fibres which are most difficult to dye with disperse dyestuffs depends on the high activation energies of diffusion, that of 2:4-dinitro-4'-hydroxyazobenzene into polyethylene terephthalate fibres being quoted<sup>7</sup> as  $-34$  kcal/mole. Hence, by raising the temperature of dyeing from  $100^{\circ}\text{C}$  to, say,  $125^{\circ}\text{C}$ , a 16-fold increase in diffusion rates is achieved as well as increased accessibility of the fibre structure. For this reason the use of high temperature dyeing equipment, which of course implies pressurized dyeing vessels, has become commonplace in the dyeing of synthetic fibres. A typical machine designed to operate in this fashion (Figure 3) is capable of dyeing up to 500 packages of yarn in one operation.

In the case of polyacrylonitrile fibres even the use of 'carriers' or high temperature dyeing equipment fails to increase appreciably the uptake of disperse dyestuffs and the only way in which this has been achieved has been by modification, by copolymerization, of the fibre structure so as to include such units as polyvinyl acetate which confer improved affinity for disperse dyestuffs<sup>9</sup>.

### Anionic Dyestuffs

Whilst disperse dyestuffs have the widest applicability to synthetic fibres they do not always possess sufficient fastness for particular end uses and on nylon especially they are unable to provide in any but pale shades the degree of fastness to washing required. It is, therefore, often necessary to employ instead anionic dyestuffs which, by the formation of salt linkages with specific chemical sites within the fibre, achieve a higher degree of fastness.

The chemical structure of nylon and that of a typical acid dyestuff are shown in Figure 4. The dyestuffs are applied under acid conditions and the mechanism by which they dye the fibre has been elucidated by R. H. PETERS<sup>10</sup> who measured the variation in saturation dye uptake with the pH of the dyebath and obtained the curve shown in Figure 5. He showed that the level of the plateau region *B* of the curve corresponded to saturation of the amine end groups of the molecular chains and that at lower pH values bonding to the amide side groupings was taking place. Since the latter was accompanied by a reduction in the mechanical strength of

the fibres, due to a break down of the hydrogen bond cross linkages between chains, a practical limit to the uptake of dye was set by the saturation of the amine groups.

Two consequences of great concern to the dyer follow from this conclusion: firstly, when dyeing a mixture of dyestuffs of differing dyeing rates the



Figure 3. High temperature dyeing equipment capable of dyeing up to 500 packages of yarn, each weighing about  $\frac{1}{2}$  lb, in one operation (by courtesy of Longclose Engineering Co. Ltd)

more rapid dyeing dyestuff may 'block' the available sites and cause difficulty in exhausting the other components of the mixture; and secondly the distribution of dyestuff throughout an assembly of fibres depends upon the distribution of amine end groups. The first of these difficulties is minimized by selection, for use in admixture, of dyestuffs having similar dyeing rates, but the second problem is less easily solved since even the most careful control of the polymer and fibre manufacture cannot prevent some small variation in chemical and physical properties still persisting and causing variations in affinity and rate of dyeing. These manifest themselves as light and dark streaks in dyed continuous filament fabrics. Again careful selection of dyestuffs can reduce the effect and very marked improvements can also be achieved depending on the method of dyeing employed.

A technique which achieves this and which is becoming increasingly widely used, because it offers the advantages of continuous processing, is to impregnate the fabric uniformly with a concentrated solution of dyestuff and subsequently heat the wet fabric to a temperature at which the dyestuffs diffuse into the fibres. This can be achieved by steaming or, more readily, in the recently developed 'Pad-Roll' machine<sup>11</sup>. The initial uniform distribution of dye on the fabric reduces any subsequent variations which may tend to develop during fixation.

Apart from the polyamide fibres, the only group of synthetic fibres to which anionic dyestuffs can be applied are those based on polyacrylonitrile in which basic groups have been incorporated by copolymerization<sup>9,12</sup>. Since all the fibres in this group are employed only in staple form—i.e. cut up into short lengths and subsequently spun into yarn in the same fashion as natural fibres—problems of irregular dyestuff uptake do not arise, such irregularities being masked by blending prior to spinning. For the same reason staple nylon fibres can be dyed readily to fast colours with suitable anionic dyes.

### Cationic Dyestuffs

One of the major groups of synthetic fibres is that based on acrylonitrile alone, of which Orlon, Dralon and PAN fibre are examples. All but the palest shades are dyed using cationic dyestuffs which, by reason of the salt linkages formed with anionic groupings within the fibre, exhibit very good wash fastness. It appears that the dyeing sites originate

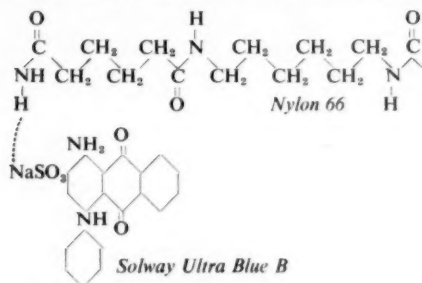


Figure 4. Chemical structure of nylon 66 and a typical acid dyestuff, Solway Ultra Blue B (I.C.I. Ltd)

in the acid catalyst employed during the polymerization process and are limited, for example, in the case<sup>13</sup> of Orlon 42 to 43 millimole equivalents per kilogram of fibre. Consequently, as in the case of nylon, there is a saturation limit to the amount of dye which the fibre can absorb and attempts to exceed this limit result in much reduced fastness to light and to washing. All these fibres, however, are marketed only in staple fibre form and hence present no problem due to varying dye uptake.

### Conclusions

One of the most surprising features of the techniques which have been developed for the coloration of synthetic fibres is that, whilst new products have been added to existing ranges of dyestuffs in order to improve fastness and other properties, no new class of dyestuff has emerged designed specifically for this outlet. Thus the reactive dyestuffs discussed by Rattee<sup>1</sup> have only very limited application to

synthetic fibres, principally because of their inability to penetrate the compact fibre structures at low temperatures. Nevertheless, the demand for improved fastness on the newer fibres is not completely

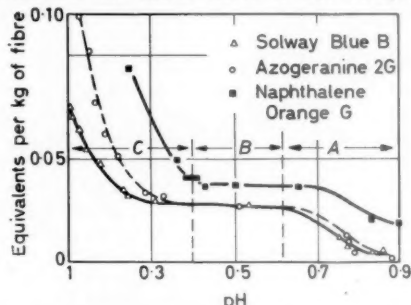


Figure 5. Variation in saturation dye uptake on nylon yarn at different pH values of the dyebath

satisfied by existing dyestuffs and there is ample scope for the introduction of new fast dyestuffs which might in addition offer greater ease of application.

Rather, the developments have been in the direction of new dyeing methods, such as the high temperature and padding techniques already referred to. The comparative ease of sublimation of the disperse dyestuffs has also led to 'ultra-high temperature' processes in which, at temperatures of 180 to 200°C, the dyestuffs are caused to diffuse into the fibres in times of the order of 15 to 60 seconds. There again one of the principal attractions is the prospect of continuous processing with its attendant lowering of labour and fuel costs.

It can confidently be expected that the challenge of new fibre types, each with its new problems for the dyer and dyestuff manufacturer, will continue to add impetus to the advancement of techniques and that, as has been the case even in the short time since synthetics first appeared, benefits will accrue to the whole of the dyeing industry.

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# THE FLOATING ZONE PROCESS

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This article describes the process by which material can be zone refined and grown into single crystals without a crucible container. The principles of the process are outlined and some of the experimental methods are described, with particular reference to semiconductor silicon; the application of the process to metals is also included. This is the eighth article in the series on semiconductors. Three others will follow: optical and other devices, and intermetallic compounds with particular reference to bismuth telluride.

THE CONTROL of impurities in a wide range of materials can be achieved by the family of methods known as zone melting<sup>1</sup>. In all of these methods a short molten zone travels slowly through a relatively long solid charge and, while travelling, redistributes the solutes in the charge. If the number, size, and travel direction of the zones as well as the initial make-up of the charge, are suitably chosen many useful operations can be performed on the charge.

The molten zone has two liquid-solid interfaces, a melting interface and a freezing interface. The zone can redistribute impurities mainly because of what happens at the freezing interface. The facts about the freezing of solutions used in the zone melting process are, of course, well known; they form the basis of the method of separation by fractional crystallization which has been used for hundreds of years. However, the technique of melting only a small part of the charge at a time, zone melting, has vastly improved the efficiency of recrystallization as a separation technique.

The first important application of zone melting was the purification of germanium for use in transistors. Its application to the purification of silicon led to a new technique called floating zone method by its originators, P. H. KECK and M. J. E. GOLAY<sup>2</sup>. Because of its reactivity when molten it is difficult to find a container to hold the silicon during the refining process. Fused silica is generally used as a container but molten silicon slowly attacks silica and the ultimate purity of the silicon so obtained is limited by the purity of the silica container. In addition, the reaction releases oxygen from the silica which then dissolves in the silicon. The floating zone technique avoids the need for any containers, the molten zone being held in place by its own surface tension between two vertical colinear solid rods of the charge material; schematic arrangements are shown in *Figures 1 and 2*.

## Principles of Operation

The stability of floating zones has been analysed mathematically<sup>3</sup>. It has been shown that the maximum length of zone that can be supported by its own surface tension increases linearly with rod radius for small radii and approaches a limit at larger radii. The maximum length that can be achieved is a function of the material the critical parameter being  $\sqrt{\sigma/\rho}$  where  $\sigma$  is surface tension and  $\rho$  is the density of the liquid zone. There appears to be no theoretical restriction on diameter when it is of the order of centimetres.

The length of the zone depends on the power required to melt the rod right through and this in turn depends mainly on the heat losses and the concentration of power which can be achieved. When power is supplied by induction heating, the levitating action arising from the repulsion between induced and inducing currents can be utilized to give additional support to the zone. The experimental conditions must be adjusted so that the midpoint of the zone lies above the plane of the induction coil. The amount of levitation obtained depends on the frequency of the induction heater and the closeness of coupling between coil and zone.

The floating zone method is particularly suited for materials which have a high surface tension and low density when molten. Examples are silicon ( $\sigma$  720 dyn/cm<sup>2</sup>,  $\rho$  2.33 g/cm<sup>3</sup>), light metals such as aluminium and denser metals of high melting point—and hence usually of high surface tension—such as iron and titanium.

When a rod of silicon is zone refined by passing a number of molten zones in the same direction along the rod the impurity distribution can be determined by solving the zone refining equation

$$C_x/C_0 = 1 - (1 - k)e^{-kx/l}$$

where  $x$  is the point on the crystal where the impurity

concentration is  $C_x$ .  $C_0$  is the original impurity concentration,  $k$  is a coefficient and is equal to  $C_S/C_L$  where  $C_S$  is the concentration in the solid, and  $C_L$  the concentration in the liquid zone;  $l$  is the length of the floating zone. For more than one pass, and taking into account the freezing out of the last zone, the calculation becomes difficult. A typical

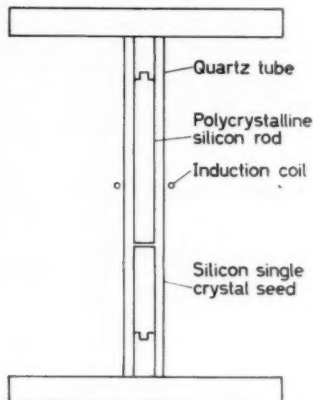


Figure 1. Schematic arrangement of the floating zone process

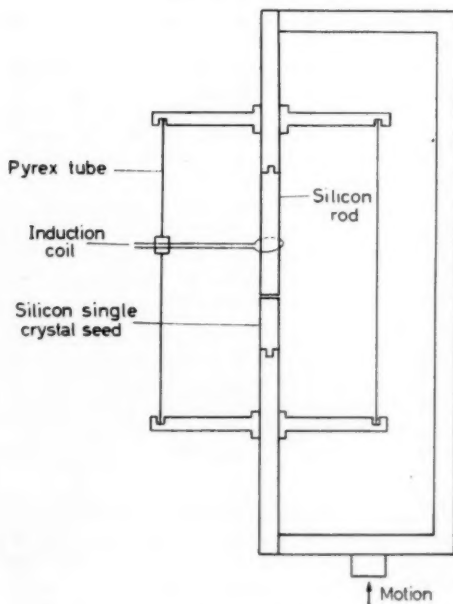


Figure 2. Schematic arrangement of the floating zone process

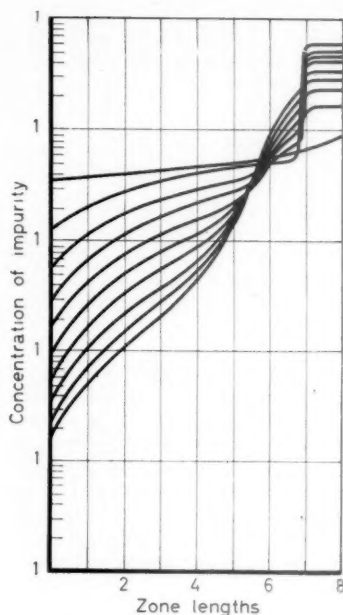


Figure 3. Calculation of phosphorus distribution for successive passes— $k = 0.35$  and  $l/L = 1/8$  (by courtesy of Du Pont)

result obtained with an analogue computer for  $k=0.35$  (phosphorous) and  $l/L=1/8$ , where  $L$  is the total length of the bar, is shown in Figure 3. This shows the distribution of phosphorus impurity in the initial crystal in the top curve and after each of nine successive zone refining passes in a bar of eight zone lengths. For the initial conditions in each curve, the impurity concentration from the previous zone is averaged over one zone width. The zone then travels along the crystal to the freezing out point producing a sudden rise in impurity concentration.

The next zone does the same until it reaches the lower edge of the higher impurity region where the previous zone froze. Here a second rise in concentration occurs due to back transfer of impurity from the higher concentration region. This goes on with each zone providing a stepwise feedback which establishes the limiting impurity concentration. The smaller  $k$  is, the more easily is the material refined. When  $k$  is large, as for boron in silicon ( $k = 0.9$ ), then another method, such as reacting the boron with wet hydrogen, must be used. Using a vacuum instead of an inert gas can change the effective  $k$  of a volatile impurity. For example, phosphorus can be removed much more rapidly from silicon under

vacuum than under inert gas, with the envelope water cooled to provide an impurity sink. In addition melting under vacuum markedly reduces the gas content of the rod.

After refining, zone levelling may be carried out. This involved sweeping a zone doped with an impurity whose  $k$  is small along the rod. The freezing interface is then crystallizing out from a molten region of effectively constant composition leading to uniform resistivity.

### Methods of Operation and Equipment

Experimentally the floating zone technique consists of melting a zone completely through a rod held vertically by a suitable chuck at each of its ends. Then the molten zone is moved smoothly at a suitable speed along the rod from one end to the other as often (in the same direction) as is necessary.

The rod must be protected from the atmosphere by an enclosure containing inert gas or vacuum. Two types of enclosure are in common use. With induction heating the work coil can be outside the enclosure as in Figure 1 or inside as in Figure 2. In the first type, where the enclosure wall is near the molten zone, transparent silica is a suitable material for the enclosure while in the second type, where conditions are less severe, pyrex may be used. A choice is available concerning the movement of the molten zone. Either the induction work coil or the rod itself can be moved. Movement of the work coil requires long and flexible electrical leads to the coil necessitating some power loss and, perhaps, some change of power output during the traverse. Moving the rod may cause some vibration of the rod. The zone is usually moved from the bottom of the rod to the top but under optimum conditions of zone size it may be moved equally well in the reverse direction.

A complete equipment for zone refining made by the Lepel High Frequency Laboratories in the United States is shown in Figure 4; it is designed primarily for production purposes. Continuously variable traverse speeds from 0.4 to 4 inches per minute upward and downward together with facilities for rotating the rod at speeds up to 50 rev/min are provided. Figure 5 shows a close up of equipment used by Du Pont at their new Brevard plant in North Carolina for zone refining silicon. Here also the work coil is stationary and the whole rod and quartz enclosure are moved through the coil.

After more than a few passes of the molten zone along the rod, the silica envelope in this type of equipment may become clouded by deposits and for laboratory use, when many passes have to be made, an equipment with a stationary envelope which bears

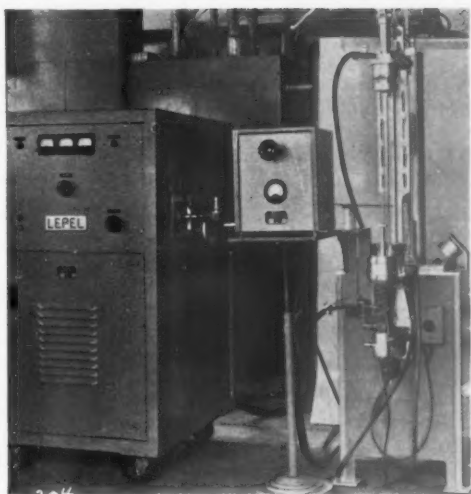


Figure 4. Production equipment for floating zone refining (by courtesy of Lepel High Frequency Laboratories, N. Y.)

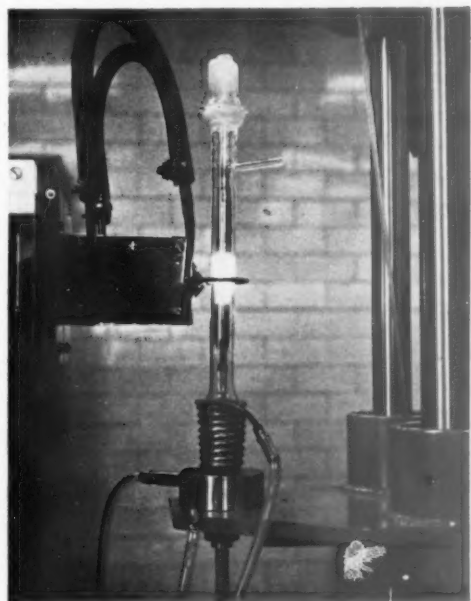
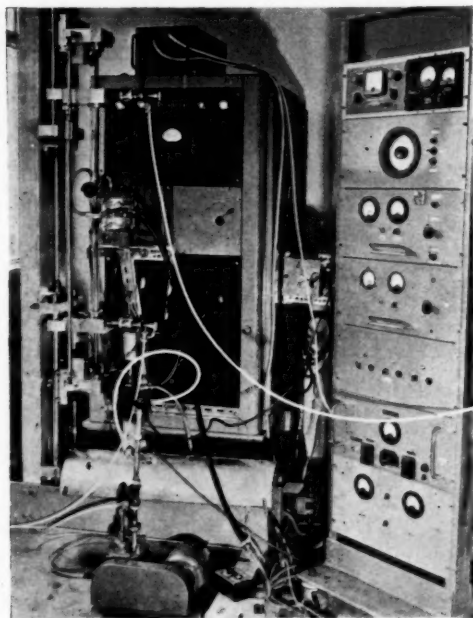


Figure 5. Silicon rod being zone refined. This equipment is being used by Du Pont in the Brevard Plant, North Carolina (by courtesy of the Editor of the Du Pont Magazine)

a sight tube side arm below which the fixed work coil is located is useful. When using wet hydrogen to remove boron from silicon there is a heavy deposit on the silica tube after the first passes and such a sight tube some four inches long enables the molten zone to be clearly observed for many passes. *Figure 6* shows an equipment of this type, built at the Royal Radar Establishment, Malvern, which has proved useful in a variety of research silicon problems.



*Figure 6. Experimental floating zone equipment (Crown Copyright Reserved)*

In this equipment the silicon rod is moved through the fixed work coil by a pair of molybdenum rods which slide through vacuum seals, one at each end of the quartz envelope. Taper chucks of molybdenum fit tapered ends of the silicon rod and provision is made for the expansion of silicon when the zone freezes out at the end of its pass along the rod. Zone travel rates are commonly 0.0005 to 0.005 inches per second and the fast return is about 0.050 inches per second. Rod rotation speeds are of the order of 5 rev/min with provision for contra rotation. This technique of contra rotation has been used successfully by G. W. GREEN at the Royal Radar Establishment to maintain straight rods of uniform diameter after very many passes.

A view of the molten zone in a silicon rod is shown in *Figure 7*. This was taken looking down the

sight tube, the axis of which in this case was at 45° to the vertical. The zone is easily recognized in silicon by its dark appearance due to the lower emissivity of the molten silicon. In order to prevent the evaporation or re-evaporation of impurities from the silica envelope, which can reduce the minority carrier lifetime in the rod<sup>4</sup>, a film of water is flowed down the outside of the envelope. This cooling water also has the useful effect of preventing any deposit from adhering too tightly to the inside of the envelope.

With silicon rods of  $\frac{3}{8}$  in. diameter, less than 1 kW of power is dissipated in maintaining the molten zone. However, power transfer conditions are such that induction units rated at 5 to 10 kW are necessary with high kVA output circuits. Two frequencies are in common use, namely 450 kc/s and 4 Mc/s. At the lower of the two frequencies more levitation is available as the efficiency of heating is less, but, as the material becomes more pure with successive zone passes it proves easier to couple in at the start of each new pass at the higher frequency. Coupling in from cold presents no problem for the silicon can be warmed by a powerful infra-red lamp, or the molybdenum chuck may be warmed by coupling into the work coil and the silicon warmed by conduction, or a heavily doped section at the impure end may be used to provide easy coupling in.

Single crystals are grown using a suitable seed provided that certain conditions are met. The zone must at all times be molten right through. Any argon or helium used as the inter atmosphere must contain less than some five parts per million of oxygen or water vapour or nitrogen, and the gas system should preferably be vacuum tight. Any scum which appears on the molten zone and affects the single crystal growth is usually corrected by improving the purity of the atmosphere. Experience shows that an inert atmosphere which proves satisfactory for the growth of single crystals of silicon by the Czochralski method will not necessarily prove adequate for the growth of single crystals in the floating zone process. Under the correct conditions a single crystal is usually obtained at the second or third pass.

Alternatively the rod may be melted by electron bombardment<sup>4</sup>. Here the electron source is a tungsten coil which surrounds the rod and is inside the enclosure as in *Figure 8*. A good vacuum inside the enclosure is also necessary. The concentration of heat input to the rod that can be achieved by this method makes it possible to apply the floating zone method to refractory materials such as tungsten and boron. Without any seeding single crystals of tungsten, rhenium, tantalum, molybdenum,

vanadium, nickel, copper, ruthenium, niobium and platinum have been made.

Although short filament life, about 100 hours maximum, is obtained—catastrophic failures may occur because of arcing or other accidents—this technique is rapidly becoming of great importance in metallurgical research. Evaporation of the filament material into the melted material, in quantities of the order of a few parts per million, is at present a limitation, but these problems will doubtless be overcome eventually by more sophisticated electron gun design.

### Achievement of the Process

This technique permits the ultimate in the preparation of pure materials which can be refined in accordance with floating zone theory. In silicon, wet hydrogen treatment followed by 67 passes has yielded material of 16,000 ohm cm resistivity corresponding to a boron level of less than  $10^{13}$  boron atoms per cubic centimetre.

For both experimental and industrial use silicon single crystals grown by the floating zone technique appear to possess several advantages over crystals grown by the present Czochralski technique of pulling from the melt. The oxygen content is much lower in floating zone crystals and this factor elimin-

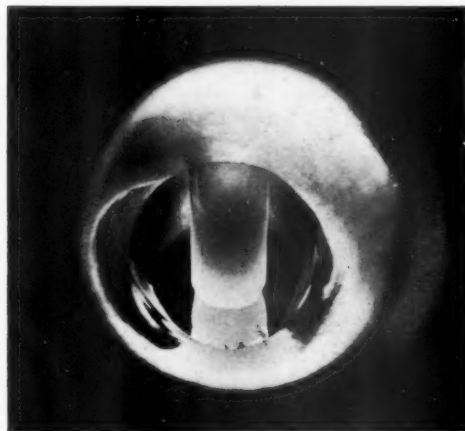


Figure 7. View of molten zone in silicon  
(Crown Copyright Reserved)

ates for these crystals many of the thermal conversion problems associated with Czochralski crystals. The perfection of Czochralski crystals tends to decrease with increasing diameter whilst the opposite seems to be true of floating zone crystals which can be grown in considerable length and with extremely small dimensional tolerance on diameter.

The material can also be purified from contamination by such elements as gold, copper, iron and manganese which may result from the chemical process or from handling the material and which can adversely affect the electrical characteristics.

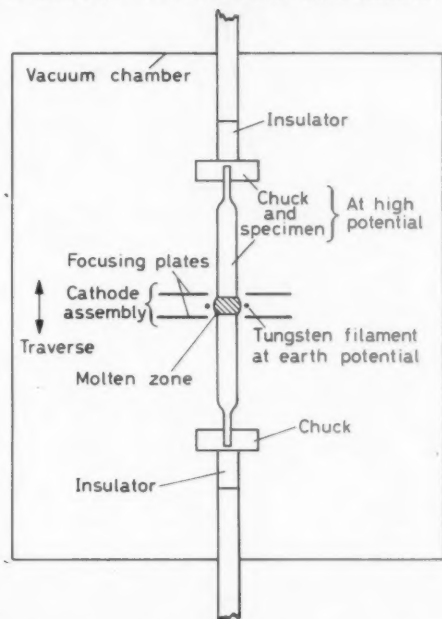


Figure 8. Schematic diagram of the apparatus used for the electron bombardment method of floating zone melting<sup>4</sup> developed by S.E.R.L. (by courtesy of the N.R.D.C.)

The technique offers an economical means of manufacturing *n*-type single crystals of high resistivity. In general resistivity and lifetime gradients are small in floating zone crystals and it is said that device yield on *n*-type material so produced is improved over yields from material produced by the Czochralski technique. In the case of metallurgical and refractory materials the demands on purity are not so severe as for semiconductor materials but already the technique has been made to yield single crystals in materials which it would be very difficult to process by more conventional methods.

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# RESEARCH

## *The 1959 Waverley Gold Medal Essay Competition*

RESEARCH is this year sponsoring The Waverley Gold Medal Essay Competition for the seventh year in succession. The Competition is designed to encourage the scientist in the laboratory and the engineer in the production plant to express his views and translate his work into an essay that will readily be understood by other scientists, directors of industrial firms and others interested in science and technology.

The **Waverley Gold Medal**, named after and bearing the coat of arms of the late Lord Waverley, together with **£100** will be awarded for the best essay of about 3,000 words describing a new scientific project or practical development giving an outline of the scientific background, the experimental results and the potential application of the project or process in industry. The essays will be judged for technical content by specialists in the subject, for clarity of presentation and for style.

A second prize of **£50** will be awarded and also a special prize of **£50** for the best entry from a competitor under the age of thirty on 31st July 1959. If the first prize is awarded to a competitor under the age of thirty, the special prize will go to the next best entry. For full details write to the Editor of RESEARCH, 4/5 Bell Yard, London, W.C.2.

**All entries must be received by the Editor not later than 31st July 1959**

# THE OIL ASH CORROSION PROBLEM

## *An Application of the Phase Equilibrium Approach*

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The inorganic impurities present in petroleum tend to concentrate in the heavy oil fraction and during combustion they form a corrosive slag known as oil ash. The author shows how this problem has been solved, largely by phase equilibrium studies and he points out that these methods could—and should—be applied to many other problems.

It is well known that many a thorny technological problem involving the behaviour of materials at elevated temperatures has yielded to a systematic study of the phase equilibrium relations in the appropriate chemical system. This type of study has greatly furthered the understanding of such diverse problems as those of Portland cement technology, steel slag chemistry, the performance of refractories, and the formation of granites. Because of the exacting and time consuming nature of such studies they have heretofore been left largely in the hands of highly trained investigators, working in specially equipped laboratories. But it is neither necessary nor desirable that activity in this fertile field of research should be thus restricted. Indeed, it is a cardinal point of the present thesis that a simple yet fruitful phase equilibrium approach to technological problems is well within the capabilities of even the most modestly equipped research or development laboratory. The approach outlined in these pages, although addressed specifically to the problem of oil ash corrosion, is believed to be of general applicability.

In the refining of crude petroleum the inorganic impurities are largely concentrated in the heavy residual fuel oil fraction. During combustion these impurities accumulate as a non-volatile and highly corrosive slag or ash. Corrosion of metal components by such ashes has become a vexing problem in the operation of the modern gas turbine engine. It is commonly agreed that the intensity of corrosion depends primarily upon the content of sodium, vanadium and sulphur in the residual ash. There has been a definite trend towards higher and higher contents of these elements in residual fuel oils over the past twenty years. The problem is therefore becoming more and more acute.

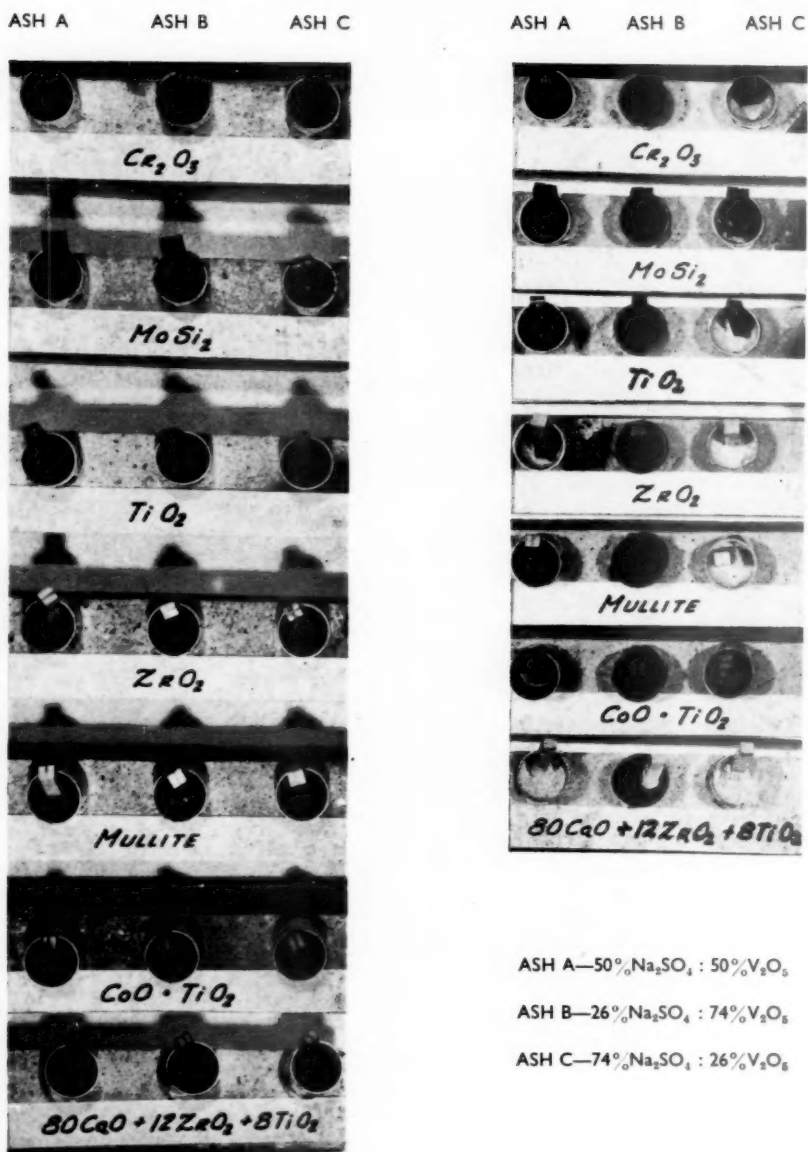
In almost all recent laboratory studies of metal corrosion by residual oil ash a simplified approach

to the problem has been made. This has involved a study of the corrosive effects of simulated ashes consisting of mixtures of sodium sulphate and vanadium pentoxide. (Figures 1 and 2 show examples of such corrosion experiments.) In view of the high contents of sodium, sulphur and vanadium in analysed ashes, such a simplification would appear to be justified. Although studies involving simulated ashes have been numerous, they have not resulted in a consistency of view as to the specific agents of corrosion. In some instances corrosion has been attributed to the influence of either or both of the end members,  $\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$ . In others, the action of one or more of a number of known sodium vanadates,  $\text{Na}_3\text{VO}_4$ ,  $\text{Na}_4\text{V}_2\text{O}_7$ , and  $\text{NaVO}_3$ , has been invoked. In still other cases the formation of complex addition compounds of sodium sulphate and vanadium pentoxide,  $\text{Na}_2\text{SO}_4 \cdot 2\text{V}_2\text{O}_5$  and  $\text{Na}_2\text{SO}_4 \cdot 9\text{V}_2\text{O}_5$ , has been postulated.

These conflicting opinions regarding the behaviour of  $\text{Na}_2\text{SO}_4$ - $\text{V}_2\text{O}_5$  ashes have precluded a clear understanding of their role in corrosion. A resolution of these discordant views would seem to constitute a necessary prelude to any successful investigation of the mechanisms involved in the oil ash corrosion process.

### **The $\text{Na}_2\text{O}$ - $\text{SO}_3$ - $\text{V}_2\text{O}_5$ System**

By fortunate circumstance, a previous study of refractories involving mixtures of dead-burned magnesite  $\text{MgO}$ , and zircon  $\text{ZrSiO}_4$ , furnished the clue which was to lead to the present successful approach to the oil ash corrosion problem. Earlier studies had interpreted these refractories in terms of simple mixtures of the two end members  $\text{MgO}$  and  $\text{ZrSiO}_4$ . Careful re-study clearly demonstrated that interaction between magnesia and zircon was of such nature that the relations could be correctly understood only by reference to the three component system,  $\text{MgO}$ - $\text{ZrO}_2$ - $\text{SiO}_2$ .



ASH A—50%  $Na_2SO_4$  : 50%  $V_2O_5$

ASH B—26%  $Na_2SO_4$  : 74%  $V_2O_5$

ASH C—74%  $Na_2SO_4$  : 26%  $V_2O_5$

Figure 1. (LEFT) Specimens placed in oil ashes prior to testing and (RIGHT) after exposure to mixtures of sodium sulphate and vanadium pentoxide for 24 hours at 871°C (1600°F).

A certain parallelism was apparent between the magnesia-zircon mixtures on the one hand, and the sodium sulphate-vanadium pentoxide mixtures on the other. Both series had been interpreted, although none too successfully, on the basis of simple two component systems,  $\text{MgO-ZrSiO}_4$  and  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$  respectively. Should interaction between  $\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$  be of such nature that reference to the three component system  $\text{Na}_2\text{O-SO}_3\text{-V}_2\text{O}_5$  would be necessary, the parallelism would be even more complete. It was this analogy, whether real or apparent, which suggested that the oil ash corrosion problem might lend itself readily to investigation against the framework of this three oxide system.

The equilibrium relations in a three oxide system are best depicted with the aid of an equilateral triangle. Each of the three oxides, for example  $\text{Na}_2\text{O}$ ,  $\text{SO}_3$ , and  $\text{V}_2\text{O}_5$ , is assigned a location at one of the three apices of the triangle. The compound  $\text{Na}_2\text{SO}_4$  (or  $\text{Na}_2\text{O} \cdot \text{SO}_3$ ) occupies an appropriate intermediate position on the side of the triangle joining the  $\text{Na}_2\text{O}$  and  $\text{SO}_3$  apices. Similarly, the compositions of the compounds  $\text{Na}_3\text{VO}_4$ ,  $\text{Na}_4\text{V}_2\text{O}_7$  and  $\text{NaVO}_3$ —or  $3\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$ ,  $2\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$ , and  $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5$ , respectively—are plotted on the side line joining  $\text{Na}_2\text{O}$  and  $\text{V}_2\text{O}_5$ . Points located in the interior of the triangle represent mixtures of all three oxides. Because of the formation of the various compounds enumerated above, these three oxides will not remain inert to one another, particularly when subjected to elevated temperatures. Rather, they will interact to yield various assemblages of oxides and compounds.

### Compatibility Triangles

Theoretical considerations developed by J. WILLARD GIBBS permit the ready determination of the maximum number of phases—gases, liquids or crystalline solids—which may co-exist in any chemical system at any random pressure and temperature. For a system such as  $\text{Na}_2\text{O-SO}_3\text{-V}_2\text{O}_5$ , no more than three such phases can co-exist under the random conditions specified. Accordingly, this three oxide system may be resolved into a number of possible three phase equilibrium assemblages. In other words, the  $\text{Na}_2\text{O-SO}_3\text{-V}_2\text{O}_5$  triangle may be subdivided into a number of so-called compatibility triangles, each of which links the compositions of three oxides or compounds which can co-exist. The simplified phase equilibrium approach followed in the present study aimed at nothing more than the delineation of the compatibility triangles corresponding to the various three phase equilibrium assemblages for the  $\text{Na}_2\text{O-SO}_3\text{-V}_2\text{O}_5$  system.

No phase equilibrium diagram of any kind had previously been drawn for this system and it was therefore desirable, as a preliminary step, to ascertain the various ways in which it could, theoretically, be subdivided into compatibility triangles. As a first step, however, it was necessary to come to a decision as to which of the recognized compounds involving  $\text{Na}_2\text{O}$ ,  $\text{SO}_3$  and  $\text{V}_2\text{O}_5$  might be expected under the conditions employed in oil ash corrosion studies. Such studies have, generally, been carried out in the temperature range  $700^\circ$  to  $925^\circ\text{C}$  and it would seem reasonable therefore to eliminate from consideration any compounds which have no stable existence in this temperature range. Sodium pyrosulphate  $\text{Na}_2\text{S}_2\text{O}_7$ , which decomposes at  $401^\circ\text{C}$ , would fall in this category, and probably also would  $\text{VOSO}_4$  and  $(\text{VO})_2(\text{SO}_4)_3$ . Elimination of these three compounds would leave only  $\text{Na}_2\text{SO}_4$  and the three simple sodium vanadates enumerated above to be incorporated in the compatibility diagram.

On the basis of the foregoing assumption that  $\text{Na}_2\text{SO}_4$  and the three sodium vanadates are the only compounds to be reckoned with, there are four distinct ways in which the diagram may be subdivided into compatibility triangles (Figure 3). One subdivision is that obtained by drawing a series of lines from  $\text{Na}_2\text{SO}_4$  to each of the compositions  $\text{Na}_3\text{VO}_4$ ,  $\text{Na}_4\text{V}_2\text{O}_7$ ,  $\text{NaVO}_3$ , and  $\text{V}_2\text{O}_5$  (Figure 3a). Another involves lines from  $\text{SO}_3$  to  $\text{NaVO}_3$ , and from  $\text{Na}_2\text{SO}_4$  to  $\text{Na}_3\text{VO}_4$ ,  $\text{Na}_4\text{V}_2\text{O}_7$  and  $\text{NaVO}_3$  (Figure 3b). A third version links  $\text{SO}_3$  with both  $\text{Na}_4\text{V}_2\text{O}_7$  and  $\text{NaVO}_3$ , and  $\text{Na}_2\text{SO}_4$  with both  $\text{Na}_3\text{VO}_4$  and  $\text{Na}_4\text{V}_2\text{O}_7$  (Figure 3c). In the fourth possibility  $\text{SO}_3$  is joined to  $\text{Na}_3\text{VO}_4$ ,  $\text{Na}_4\text{V}_2\text{O}_7$  and  $\text{NaVO}_3$ , and  $\text{Na}_2\text{SO}_4$  is linked to  $\text{Na}_3\text{VO}_4$  (Figure 3d).

Theoretically, only one of these configurations can be valid under the conditions prescribed for the oil ash corrosion tests, and there is no readily apparent reason why any one should be chosen in preference to the other three. However, a few judiciously planned experiments should lead to the elimination of three of the possibilities and the remaining configuration should faithfully depict the compatibility relations in the system for the given conditions.

It will be recalled that oil ash corrosion studies have almost invariably utilized simulated ashes composed of mixtures of  $\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$ . The compositions of these mixtures, of course, fall in the interior of the three oxide system. Such mixtures, when heated to temperatures in the range  $700^\circ$  to  $925^\circ\text{C}$ , should conform to the compatibility relations which are valid for the  $\text{Na}_2\text{O-SO}_3\text{-V}_2\text{O}_5$  system in that temperature range. Identification of



Figure 2. Crucible tests showing corrosive effects of selected ashes on a cobalt-titanium carbide cermet (20 Co-80 TiC) after 24 hours at 871°C (1600°F)

the oxides and compounds present in the various mixtures after such heat treatment should therefore permit the selection of the one valid compatibility diagram from the four theoretical possibilities. However, due to the absence of published data covering the optical properties and x-ray diffraction patterns of a number of the compounds involved, reliable identification was not feasible.

#### Selection of Valid Compatibility Diagram

At this juncture a highly significant observation was made, which indicated the possibility of an indirect solution to the problem. This observation had to do with the weight losses to be expected from  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$  mixtures on the basis of each of the four possible compatibility configurations. For the first possibility the line joining  $\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$  signifies that these two end members are compatible. Accordingly, no interaction should occur when the mixtures are heated, nor should any weight loss be encountered. For each of the other three configurations, however,  $\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$  are shown to be incompatible. Consequently, interaction should occur between them, resulting in the production of one or more sodium vanadates, and accompanied in each instance by the evolution of gaseous  $\text{SO}_3$ . Three of the compatibility arrays are alike, then, in as much as each predicts weight losses for the interacting  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$  mixtures. They are unlike, however, in the amount of the weight loss which they predict for any given mixture. The differences are strikingly revealed when theoretical weight losses are plotted against composition for each of the three configurations (Figure 4). The prospects therefore appeared promising and careful weight loss experiments might lead to the correct selection of the valid compatibility diagram.

The next logical step was to heat a series of  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$  mixtures, and, after careful weight loss measurements, to determine if the results could be correlated with one of the theoretical weight loss

curves; the apparatus used is shown in Figure 5. Accordingly, eight carefully weighed mixtures were subjected to prolonged heating at 870°C, and weight losses were determined after 24 and after 120 hours. The observed weight losses were plotted against original composition, and compared with weight losses calculated on the basis of each of the four compatibility arrays. The result of this comparison was striking: observed losses showed a remarkably close agreement with one, and only one, of the calculated weight loss curves. An apparent discrepancy, in the form of unexpected weight losses from  $\text{V}_2\text{O}_5$  samples, proved to be due to 'creep' of molten  $\text{V}_2\text{O}_5$  from the crucible, rather than to loss by volatilization. On the whole, the results pointed to a choice of compatibility diagram which would appear to be unequivocal. The diagram thus indicated to be valid was that in which  $\text{SO}_3$  is linked to  $\text{NaVO}_3$ , and  $\text{Na}_2\text{SO}_4$  is linked to all three sodium vanadates (Figure 3b).

It is well to emphasize at this point that the selection of the proper compatibility diagram was based solely on the indirect evidence of weight losses. This is a departure from the established practice, in which compatibility relations are established on the basis of careful identification of the of existing compounds. As previously noted, the lack of diagnostic data on the various compounds rendered this method at first impractical.

#### X-Ray Diffraction Evidence

It was felt that the reliability of the weight loss method might be open to question, unless supported by some such confirmatory evidence. Accordingly, it was deemed advisable to obtain reference samples of each of the compounds involved, and to secure therefrom a series of standard x-ray powder patterns. The heat treated  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$  mixtures were also subjected to x-ray diffraction analysis, and the resulting patterns were carefully compared with the standard patterns. The results were gratifying:

$\text{Na}_2\text{SO}_4$  and  $\text{V}_2\text{O}_5$  were never found in the same mixture, thus attesting to their incompatibility. In mixtures towards the  $\text{Na}_2\text{SO}_4$  end of the series  $\text{Na}_2\text{SO}_4$  was accompanied by  $\text{NaVO}_3$ , but never by  $\text{Na}_3\text{VO}_4$  or  $\text{Na}_4\text{V}_2\text{O}_7$ . Obviously, some of the  $\text{Na}_2\text{SO}_4$  had reacted with the  $\text{V}_2\text{O}_5$  to form one, and only one, of the three sodium vanadates. There can be little doubt, after the weight loss experiments, that a gas was evolved in the process, and that this was  $\text{SO}_3$ .

Thus far, weight loss and x-ray data were in accord. Complications were encountered, however, towards the  $\text{V}_2\text{O}_5$  end of the series. The compatibility diagram selected on the basis of weight losses, if strictly adhered to, would require that mixtures rich in  $\text{V}_2\text{O}_5$  should contain both  $\text{NaVO}_3$  and  $\text{V}_2\text{O}_5$ . But the corresponding x-ray patterns were not in agreement with this expectation. Instead, the diffraction peaks of either  $\text{NaVO}_3$  or of  $\text{V}_2\text{O}_5$  were

joined by many additional peaks which could not be assigned to either of these phases. The conclusion was inescapable that one or more additional compounds must be involved in the system. Furthermore, the incompatibility of  $\text{NaVO}_3$  and  $\text{V}_2\text{O}_5$  indicated that the selected compatibility diagram was, at best, only partially correct.

In an attempt to elucidate the unexpected complications noted above, an additional group of closely spaced  $\text{Na}_2\text{SO}_4$ - $\text{V}_2\text{O}_5$  compositions near the  $\text{V}_2\text{O}_5$  end of the series was prepared and heat-treated. Careful scrutiny of the x-ray patterns indicated that two additional compounds were present. Correlative study of  $\text{Na}_2\text{O}$ - $\text{V}_2\text{O}_5$  compositions revealed the same two compounds, and established  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$  and  $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$  as the most probable formulas. Closer examination of the second of these compounds raised some doubt as to its identity with the simple formula,  $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ . Upon crystallization

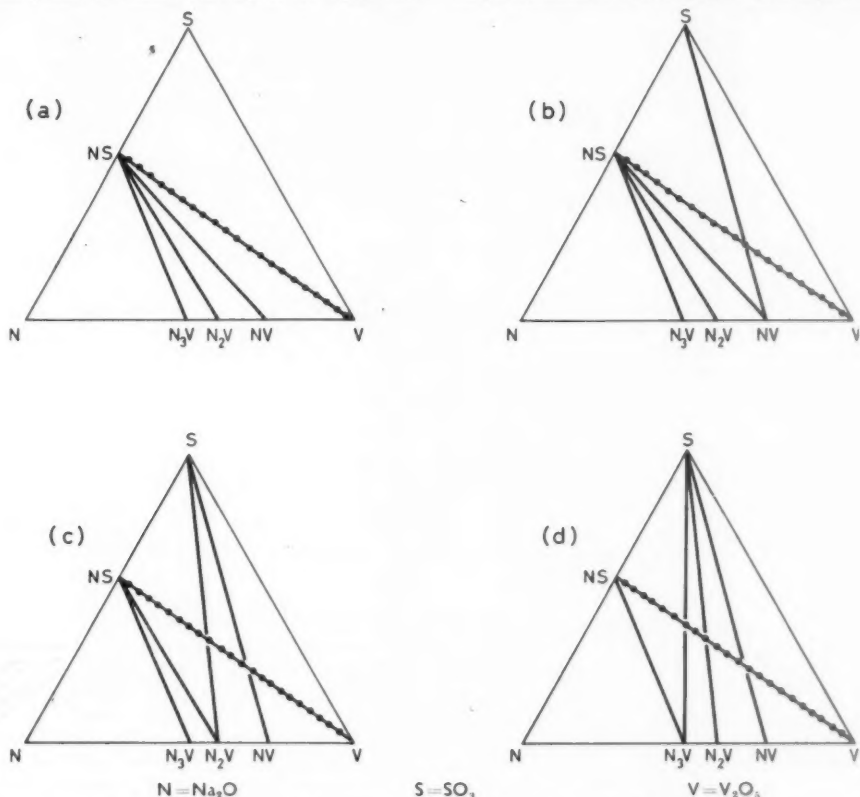


Figure 3. Four possible compatibility diagrams (in wt.%) for the system  $\text{Na}_2\text{O}$ - $\text{SO}_3$ - $\text{V}_2\text{O}_5$ . Simulated ashes fall on dotted line

from the molten state, oxygen was evolved, only to be reabsorbed upon fusion. On the basis of this peculiar 'breathing' phenomenon, and after determination of the accompanying weight change, it was concluded that the formula for the molten material was  $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ , whereas that for the crystalline solid was  $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 5\text{V}_2\text{O}_5$ . A compound with this formula has long been known to exist.

Despite the oxygen deficiency, it does not seem amiss to regard the compound as  $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$  for the purposes of the present study, and to include it as a bona fide compound on the  $\text{Na}_2\text{O}-\text{V}_2\text{O}_5$  side-line of the triangle. If the  $\text{SO}_3$  apex is joined to the  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$  and  $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$  compositions, the earlier selected compatibility diagram becomes complete (Figure 6). An additional dotted line, joining  $\text{Na}_2\text{S}_2\text{O}_7$  to  $\text{NaVO}_3$ , would have significance only at temperatures below  $401^\circ\text{C}$ , the decomposition point for sodium pyrosulphate.

### Some Conclusions

What significance, one may well ask, does this compatibility diagram have for the oil ash corrosion problem? Strictly speaking, the diagram depicts

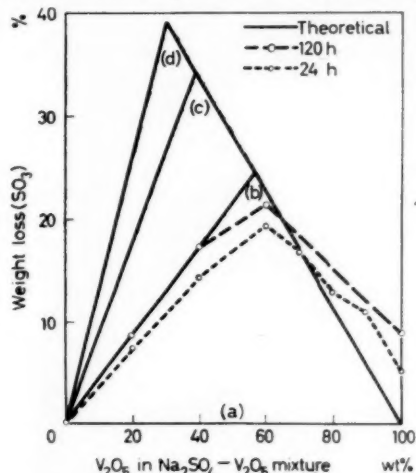


Figure 4. Experimental weight losses from  $\text{Na}_2\text{SO}_4-\text{V}_2\text{O}_5$  mixtures at  $871^\circ\text{C}$  ( $1600^\circ\text{F}$ ) and theoretical weight losses on the basis of (a), (b), (c) and (d) in Figure 3

compatibility relationships between phases which, with the exception of  $\text{SO}_3$ , are crystalline solids. Yet investigators of the oil ash corrosion problem are in agreement in insisting that appreciable corrosion occurs only when the ash is wholly or largely molten. Hence the objection might

reasonably be raised that compatibility relations found to exist between crystalline compounds may have little or no significance for completely molten materials. Such an objection might not readily be

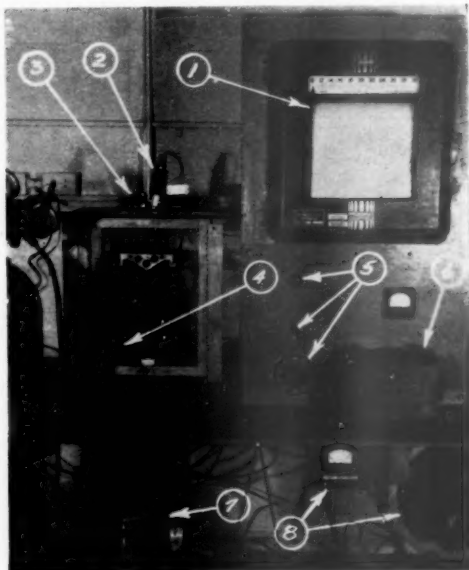


Figure 5. Automatic weight change recording equipment showing various components—(1) strip chart recorder; (2) illumination source; (3) photocell; (4) control solenoid; (5) range adjustments; (6) potentiometer (temperature measurement); (7) furnace; and (8) furnace controls

refuted to the complete satisfaction of all. Attempts to do so would necessarily involve consideration of the structure of liquid solutions, a subject fraught with considerable controversy.

There is, however, steadily mounting evidence that molten materials retain substantially the types of linkage present in the corresponding crystalline compounds. Certainly, molten  $\text{Na}_2\text{SO}_4$  does not behave in corrosion studies as if it were merely a solution of  $\text{SO}_3$  in molten  $\text{Na}_2\text{O}$ , nor do the molten compositions corresponding to  $\text{NaVO}_3$ ,  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$  and  $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$  behave as if they were merely mutual solutions of  $\text{Na}_2\text{O}$  and  $\text{V}_2\text{O}_5$ . Indeed, the unusually severe corrosion produced by molten  $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$  would defy explanation on the basis of the mutual solution theory. On the other hand, it augurs well for the belief that the structural differences between the molten and the crystalline conditions of a compound or mixture of compounds are differences of degree rather than of kind. The fact that molten  $\text{Na}_2\text{SO}_4$  does not

evolve  $\text{SO}_3$ , whereas molten  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$  mixtures do, might at first glance appear to have little significance in this connection. But this fact assumes considerable import when it is realized that molten  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$  mixtures lose  $\text{SO}_3$  in strict accordance with prediction based on solid state compatibilities.

In keeping with the foregoing line of reasoning it is believed that the compatibility relations deduced for the system are essential to a fuller understanding of the role of sodium, sulphur and vanadium in oil ash corrosion. Acceptance of this belief leads to considerable clarification of the behaviour of  $\text{Na}_2\text{SO}_4\text{-V}_2\text{O}_5$  mixtures, and to the resolution of a number of apparent conflicts. The chemical entities which emerge from this study as potential agents of corrosion are:  $\text{Na}_2\text{SO}_4$ ,  $\text{SO}_3$ ,  $\text{NaVO}_3$ ,  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ ,  $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$  (or  $\text{Na}_2\text{O} \cdot 6\text{V}_2\text{O}_5$ ), and  $\text{V}_2\text{O}_5$ .

The agents present in any given ash can readily be determined from the diagram. The latter indicates that a mixture must contain in

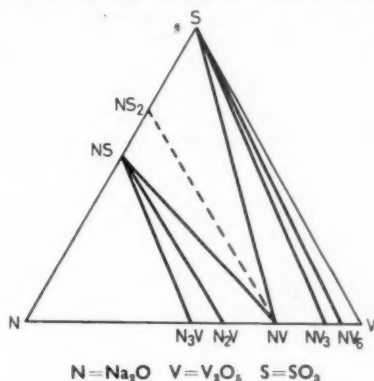


Figure 6. Compatibility relations in the system  $\text{Na}_2\text{O-SO}_3\text{-V}_2\text{O}_5$

excess of 89 per cent of  $\text{V}_2\text{O}_5$  in order for free  $\text{V}_2\text{O}_5$  to be present. Since analysed ashes seldom contain more than 80 per cent  $\text{V}_2\text{O}_5$ , it is difficult to see how the free oxide is of much consequence in corrosion, despite frequent suggestions in its favour. On the other hand,  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$  and  $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$  take on a singularly important role in corrosion. The perplexing observation of several investigators, that mixtures containing 80 to 85 per cent  $\text{V}_2\text{O}_5$  are usually corrosive, is apparently to be attributed to the presence of one or both of these compounds. The need for greater attention to the possible role of  $\text{SO}_3$  in high temperature

corrosion is also high lighted. Such postulated compounds as  $\text{Na}_2\text{SO}_4 \cdot 2\text{V}_2\text{O}_5$  and  $\text{Na}_2\text{SO}_4 \cdot 9\text{V}_2\text{O}_5$  have failed to appear, and may safely be discarded as non-existent. The compounds  $\text{Na}_3\text{VO}_4$  and  $\text{Na}_4\text{V}_2\text{O}_7$  may be eliminated from consideration for present purposes. The diagram indicates that they can form only if free  $\text{SO}_3$  is absent, a stipulation which is met neither by simulated nor actual ashes. It is of interest to note that the results of the examination of actual oil ashes are in accord with present findings. Thus,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_2\text{O} \cdot 3\text{V}_2\text{O}_5$ , and  $\text{Na}_2\text{O} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5$  have all been identified by x-ray diffraction. There appears to be considerable doubt, however, as to whether free  $\text{V}_2\text{O}_5$  as such has been detected in such deposits.

Other investigators of the oil ash corrosion problem, when apprized of the findings presented in the preceding pages, have welcomed the approach for the new light which it sheds on a difficult problem, and for the order which it introduces into the confusion which had previously existed. The high hopes held out at the inception of the investigation would thus appear to have been realized. Yet it must be admitted that little more than a beginning has been made. In its relation to the overall problem of oil ash corrosion the present study, far from providing the answer, has merely helped to clarify the question. But its significance need not reside merely in the clarification of previous work. Rather, this approach should furnish a useful framework for more extended corrosion studies.

Much remains to be learned in regard to the identity of the products of oil ash attack on metals and alloys, the relative merits of various additives in mitigating the intensity of attack, and the establishment of the mechanisms involved in the corrosion process. Investigations in each of these areas have already been launched as logical extensions of the present study. Although still in progress, these have already met with encouraging results. In conclusion, the general method of approach is recommended as a simple yet promising aid in the solution of other high temperature technological problems.

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# SCIENCE IN PARLIAMENT

## Navigational Aids

There is often complaint, with every justification, that questions are asked in Parliament that could more quickly and accurately be answered by consulting the appropriate textbook or qualified librarian. But sometimes not enough questions are asked. One such case in point is the matter of the United States VOR-DMET air navigation system or the British Decca radar system. It has been almost universally agreed that the latter is cheaper, safer and better but are American business interests to be allowed to triumph with only a small murmur?

Both Mr JOHN HALL (Conservative, Wycombe) and Mr W. J. PEEL (Conservative, Leicester, S.E.) questioned the Minister of Transport and Civil Aviation on why the International Civil Aviation Organization had decided to adopt the former. The reply from the Ministry was that 'present standards of safety, in congested air space, cannot be maintained with the use of the VOR-DMET system without seriously reducing the efficiency of air traffic control. For this reason the Government will continue to press for a more satisfactory solution'. Later Mr WATKINSON himself replied to further questioning (18th March) and he endorsed and enlarged on the opinion given previously.

Science or politics, which will triumph?

## Fog Dispersal

Fog or smog, whichever one cares to call it, is not only unpleasant, but also very costly. Costly in terms of transport delays, working time and health. Both the Parliamentary Secretary to the Minister of Supply and the representative of the Minister of Transport and Civil Aviation in the House were questioned on this matter by Mr R. MASON (Labour, Barnsley). To what extent had researches been conducted on fog dispersal?

Mr W. J. TAYLOR (Conservative, Bradford, N.) for the Ministry of Supply said (16th March) that F.I.D.O. still appeared to be the most promising method and it was hoped that it might eventually be suitable for both civil and military aerodromes. Although the Meteorological Office tests were being continued in various localities, it was not considered that this method had much prospect of success.

Mr J. RANKIN (Labour, Govan) pointed out that the Air Corporations had lost over £200,000 last winter solely due to fog—a very formidable sum for any business concern. 'When may we expect that

this method of dispersing fog will be in operation as we have now been experimenting for nearly ten years?' Mr Taylor replied that F.I.D.O. was still much too expensive, about £150 to £250 per landing.

In contradiction to the earlier reply by Mr Taylor, Mr A. NEAVE (Conservative, Abingdon) for the Secretary of State for Air said (18th March) that the Meteorological Office tests, at present at the field trial stage, on the possibility of 'extracting moisture from the air over limited areas by spraying with chemical solutions' had shown some promise. (This is, in fact, a method of coalescing moisture into larger droplets which will then fall as rain.) The battle—and one could almost call it that—was resumed by Mr A. ALBU (Labour, Edmonton) on the 23rd March, dealing again with the question of the fog dispersal method developed at Battersea College. 'Why did it not justify further development?' Mr Taylor said that the method—a means of accelerating the rate of coalescence of the minute water droplets by spraying with a surface active agent using an aeroplane for the purpose—showed no promise.

Mr Mason had the last word: 'More fog'.

## Use of Coal

The Postmaster General, Sir IAN HOROBIN, recently dealt with two sets of questions about how we can best use our coal resources. At the moment there was, unfortunately, a surplus of coal and it was suggested that low temperature carbonization of coal to produce oil, chemicals and smokeless fuel might provide the answer.

In reply to the Hon. PATRICK MAITLAND (Conservative, F. Lanark, 9th March), Sir Ian said that the Scientific Advisory Committee had been asked if it were possible to increase research into practical processes for the production of oil, gas and chemicals from coal. Substantially the same question was asked by Mr J. GEORGE (Conservative, Pollok, 16th April) by which time Sir Ian was able to inform the House that a committee had been set up, under the chairmanship of Mr. A. H. WILSON, F.R.S., which was to review the work done over recent years on the development of processes in which coal is the raw material and which will produce marketable products such as chemicals, gaseous or liquid hydrocarbons. The committee is also to make recommendations on the direction further research and development work on any such process should take and to suggest which processes they thought held the best promise of speedy industrial application.

## SURVEY

### Photoelasticity

A jubilee commemoration of the work of Professor E. G. COKER and Professor L. N. G. FILON was held at University College, London at the end of April. It is about fifty years since these two research workers first met and began their development of photoelasticity. This collaboration lasted for over twenty-five years and resulted in the production of a method of experimental stress analysis which has been extensively used, first in the design of aircraft components and latterly in many other engineering applications.

Coker was an engineer solely concerned with the practical applications of this technique and perhaps was rather impatient with the amount of theoretical work that was needed in order to turn this piece of pure research into a practical working tool. Filon was the mathematician who worked out the theory of photoelasticity and together these two pioneers laid the complete foundations of the technique of using photoelasticity to investigate the behaviour of actual structural materials. Many improvements have, of course, been made but their technique was substantially that still used today.

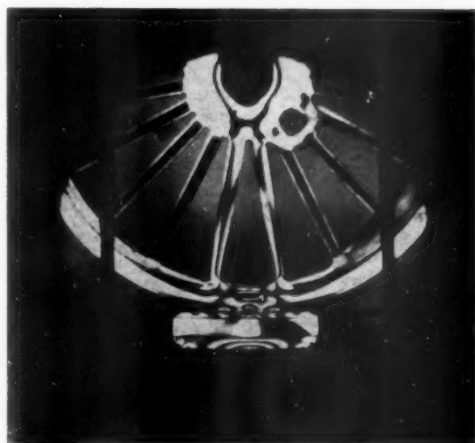


Figure 1. Coker's original model of a locomotive driving machine showing the stress pattern (by courtesy of the Department of Civil Engineering, University College, London)

At University College the exhibits ranged from some of the old apparatus used by Coker and Filon—the stress pattern produced by Coker's original model of a locomotive driving machine is shown in

Figure 1—to examples of the current work of the Department in testing the stresses produced on aircraft components with different types of loading and stresses produced on such apparently simple things as the walls of grain silos.

### Engineering Exhibition at Olympia

The Engineering, Marine Welding and Nuclear Energy Exhibition was held at Olympia, April 16th to 30th, 1959. The Exhibition has now become a regular event on the calendar of most engineers and, as with all traditional events, it is difficult to find the 'new' items on exhibition. It is, of course, always exciting to see new things, to hear about new developments, but exhibitions are designed to sell, and the bread and butter of industry is still the solid traditional equipment, the large piles of steel plate and the various types of industrial engines. It is true that a lot of these have changed their face considerably with both major and minor modifications, modifications that all but the expert find it difficult to assess. Two items that seemed relatively new did catch the eye of many visitors.

The first was a design of a nuclear reactor for ship propulsion that was being built for the *Savannah*\* by the American company of Babcock and Wilcox. A conversation with the staff on the stand revealed that in fact Babcock and Wilcox had undertaken design studies of suitable ship reactors in this country and—should anybody wish to order a nuclear powered ship—they would be very willing to build one. They had considered both the gas cooled reactor and the pressurized water reactor and on the whole favoured the latter. They felt that the large mass of graphite in the former was undesirable on a ship liable to roll in heavy seas but, on the other hand, the pressurized water reactor would need a large containment vessel, probably of welded one inch mild steel, to avoid any accidents should the ship be involved in a sudden collision or receive a sudden shock. Babcock and Wilcox claimed that the weight of the reactor and shielding, including the biological concrete shield, would be less than the weight of oil that a large vessel would need to carry if travelling between Aden and the United Kingdom via the Cape without stopping. The probability was that the most economical application of nuclear propulsion would be for tankers carrying cargoes non-stop over long distances; a

\* See 'Nuclear Propulsion' by J. EDWARDS in the January issue of *RESEARCH* (page 26)

nuclear reactor would be very uneconomical for passenger liners which made frequent stops.

Another interesting exhibit was a range of frictionless bearings made by the United Steel Companies in, of all surprising materials for a steel company, resin bonded fabric. The material has exceptionally low friction properties and will work

Table 1. Frictional properties of Orkot—coefficients of friction for roll coverings and rollers

Lubricant	Coefficient of friction Rubbing speed 90 ft/min. Load 2240 lb/sq. in.
Water and aqueous solutions	0.004—0.008
Soluble oils	0.013—0.017
Grease/water	0.014—0.018
Oils	0.015—0.019
Greases	0.055—0.065
Dry on steel	0.21
Dry on aluminium	0.32

in water, aqueous solutions, oils and greases. It can also be used with mild alkali but is not advised for strong alkali (see Table 1). On the other hand when dry, as show in Table 1, Orkot has a good grip and is suitable for driving rolls. It has been used for bearings, bushes, rolls and roll coverings in applications where the running temperatures are not much above 100°C. It is not suitable for higher temperatures because of the fabric employed and, apparently, if this fabric is replaced by a material such as glass fibre the advantageous frictional properties are entirely lost.

### New Process for Dyeing Wool

Recently, a new and simple method for dyeing wool has been described\*. Loose wool is placed in a dye bath containing a solution of the dye in formic acid and the dyeing process is completed in about one or two minutes at room temperature. The more nearly anhydrous the formic acid—although commercial 85 to 90 per cent acid is quite satisfactory—the faster the process and it is claimed that micrographs show a completely uniform dye uptake.

The importance of this method lies in the fact that the majority of conventional processes require higher temperatures, about 50° to 60°C, and/or longer immersion times during which the wool fibres are often damaged. The process has been tested on a fair range of commercial dyestuffs and is effective with acid dyes, neutral-dyeing 1:2 metal complex

dyes and the Cibacron (Ciba) dyes but is, as expected, unsuitable for basic dyes. Preliminary experiments have shown that the special action of the formic acid solvent is due to various favourable effects which fortunately occur simultaneously.

The main application will probably be in the continuous dyeing of loose wool or tops, for the wool industry is anxious to develop continuous processes where these can be applied. Formic acid solutions are unsuitable for high twist yarns—the swelling of the twisted fibre prevents penetration—but pieces of fabric have been printed with a thickened formic acid dye solution. The commercial aspect does, of course, depend on the easy recovery of formic acid and this appears to be quite promising. (The whole work forms part of the general programme of the Division of Protein Chemistry, C.S.I.R.O. on the structure and chemistry of wool. Some of the results of this work were reviewed on page 82 of the March issue of RESEARCH.)

### Miniature Solid Circuits

It has been accepted that all electronic devices do become progressively smaller—just as aeroplanes become faster or bigger or both—and the grey boxes have more and more 'electronics' crammed inside the same space. Dare it be said that this process of miniaturization has approached its limit? Texas Instruments have now developed a complete semiconductor solid circuit with diodes, transistor, resistances and capacitances no larger than a match head!

Two of these circuits were recently shown in the United States. The first was a multi-vibrator circuit containing, as integral parts of the semiconductor material, the equivalent of twelve electronic components—two diffused-base transistors, two capacitors and eight resistors. The second was an oscillator circuit containing the equivalent of nine components, one transistor, three capacitors and five resistors. These miniaturized circuits are called micro-modules. The diodes, transistors, resistors and capacitors are formed as integral parts of single pieces of semiconductor material, either silicon or germanium suitably doped. It is expected that they will be able to achieve densities of the order of five hundred thousand components per square foot, an increase of the order of  $\times 10^2$  to  $\times 10^3$  compared with printed circuits.

The new solid circuits are expected to find greatest potential application where large numbers of repetitive circuits are required, such as in computers, for rockets, missiles, satellites and all micro-instruments where weight, size and extreme reliability are the critical factors. It is claimed that the production tech-

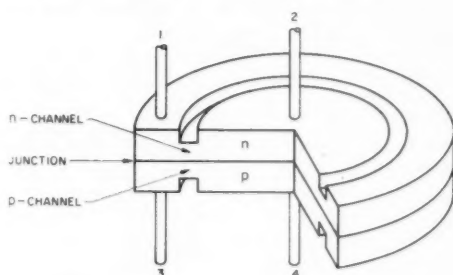
\* HARRAP, B. S. *J. Soc. Dyers & Colourists* (1959) 75, 106; *Austral. Pat. Appln* 38731/58.

niques which have been developed give a more reliable product because, in addition to more accurate process control, the devices are designed for specific applications and have very many fewer leads and connections. The devices actually exhibited are still development models, but production is expected to start within the year.

### Versatile Semiconductor Tetrode

A new kind of semiconductor device which appears to have no analog functionally, either in thermionic valves or in previous semiconductor devices has recently been developed by the Bell Telephone Laboratories in the United States. The geometry of the device seems to be quite simple. It consists of a disc of semiconductor material with a diffused junction shown schematically in *Figure 2*. A circular groove is cut and etched on each side of the disc to within about one thousandth of an inch of the junction and two leads are attached to each face of the disc, one inside and the other outside the groove. When a voltage is applied across the junction, the thickness of the depletion layer adjacent to it is either increased or decreased, depending on the direction of the biasing voltage, and this in turn increases or decreases the resistance of each 'channel' between the bottom of the groove and the junction.

It is thought that one of the most important applications of this tetrode will be as a distortionless modulator, or electronically controlled resistor for large signals. In this case, a relatively low frequency control voltage varies the width of the depletion layer and therefore the resistance of the tetrode. If



*Figure 2. Schematic illustration of the field effect tetrode developed by Bell Telephone Laboratories—the numbers refer to the four leads*

the frequency ratio is maintained at a high level, simple capacitors act as high pass filters to isolate the control voltage from the signal. The signal

voltage does not appear across the junction, it has no effect on the depletion layer and it can thus be magnitudes higher than the control voltage without being distorted by self-modulation. Similarly it is not limited by junction capacitance. The device will also function as a transformer or gyrator and, when correctly biased, will act as an isolator allowing the passage of alternating current in one direction only.

If the inner lead on one face and the outer lead on the other are connected, the tetrode will function as a two terminal a.c. short circuit stable negative resistance and, in laboratory experiments, this has been achieved over the range 30 to 250 V at 0.6 to 0.1 mA using a boron doped silicon crystal with a phosphorus diffused junction.

The practical development of the device is still at a very early stage—so far these field effect tetrodes have only been produced in the laboratory—but in laboratory experiments it has performed certain functions that previously could only be achieved by extensive circuitry.

### Hypersonics

Sound waves with a frequency of about 10,000 million cycles per second have been produced by Dr E. H. JACOBSEN of the General Electric Company (U.S.A.). This frequency is about one million times greater than the highest pitch the human ear can detect and many factors higher than the ultrasonic waves used in non-destructive testing and cleaning of metal components.

These ultra-high frequency ultrasonic waves will be used as a research tool, for research into the solid state—energy levels of atoms and interaction of electronic spins, the crystal lattice—for they should prove to be 'one of the most effective methods yet for "shaking-up" the atoms in solids'. The sound waves were created by applying microwave pulses to a quartz crystal in a cavity-resonator specially designed for the purpose and maintained at 2°K.

### Transient Storage Oscilloscope

A new unit, the Remscope, has been put on the market by Cawwell Research and Electronics Limited. This has a number of unique and rather interesting features. The instrument uses an English Electric E702 storage and display tube which has a much faster response than the American 'Memotron' cathode ray tube previously used. The E702 contains a storage system which allows transient signals to be stored for up to one week and displayed for a limited period during that time. In the case of the Remscope this time is about 15 minutes spread over a week; on

all but the fastest signals this time may be extended to about two hours with a slight reduction of brightness. Display is, of course, delayed until required or, alternatively, it may be switched on automatically when a signal is received.

The persistence of the display can be varied from a few seconds up to about 15 minutes at a time and is particularly useful when comparing one event with its predecessor in a series. Adjustment can be made so that the first signal is made to fade as the third appears and so on. Variation of the setting will allow other sequences to be produced. The erasure is rapid and is obtained by depressing an internal press-button or making an external circuit.

The accuracy of the instrument is, as expected, that of a high grade oscilloscope and a provisional price of £625 has been published.

### Computer to Translate into Braille

The American Printing House for the Blind together with mathematicians from I.B.M. have adapted a standard IBM 704 computer so that it will translate printed texts from English into Braille. A book of 300 pages can be translated in one hour, a task that would take a skilled translator at least six days.

Braille consists of 63 combinations of six raised dots which represent not only letters of the alphabet, numerals and punctuation marks but also 183 special contractions and abbreviations somewhat similar to those used in shorthand. The texts to be translated are put on to punched cards which are in turn fed into a computer, previously programmed for the conversion of English into Braille. The computer can carry out as many as 600 instructions per word in less than one fortieth of a second. Contractions and abbreviations are checked by matching the letters involved against an alphabetical table of Braille equivalents. The translated text emerges from the computer in the form of coded symbols on punched cards and these are then passed to the printer unit, attached to the computer, which reproduces Braille symbols above the English text. The reproduction of both Braille symbols and English text is required for editing purposes and, after editing, the correct punched cards are fed into a machine which produces metal plates suitable for use on a rotary press.

This development will make many school and technical books, now rarely translated into Braille, readily available and it will therefore increase the career possibilities of blind persons. To speed this translation, I.B.M. have agreed that printed texts will be recorded on magnetic tape and distributed

to I.B.M. computer installations where they will be translated and the cost borne by I.B.M.

### Heliport for London

Helicopters will now have a planned home in the Central London area. The new Heliport built by Westland Aircraft Limited at Battersea was formally opened on April 23rd by Mr John Hay, M.P., Joint Parliamentary Secretary to the Minister of Transport and Civil Aviation. The Heliport has a T-shaped landing platform built over the river bed and can accommodate the largest types of British and American helicopters currently in existence such as the Westland *Westminster* and the Fairey *Rotodyne*. At a later date a lighting system will be installed to enable the Heliport to be used at night. Services will include radio communication, navigational aids, refuelling, towing and parking facilities for six medium-sized helicopters. Fire fighting facilities are, of course, provided.

The Heliport is initially being operated under private licence and operators will be required to give some prior notice of their intention to use it. Bristow Helicopters Limited are operating a helicopter taxi service for passengers and freight which can be used in the same way as a taxi or car-hire service. At present the service which will use Westland *Widgeon* four-seater helicopters, will be confined to daylight but night flights will certainly be operated at a later date. It is expected that the helicopters will be hired—the present charge is £40 per hour—for the transportation of personnel between city centre and factory site or city centre and airport. They can, of course, also be hired for other purposes, such as aerial photography, sight-seeing trips, publicity and advertising.

### Standard of Time: an Award to Dr Essen

Dr ESSEN, Senior Principal Scientific Officer, National Physical Laboratory, has been given the Wolfe Award for the year 1959. The award, a cheque for £500, is the first of ten annual awards to be made under the terms of a will to a research worker who is considered by the D.S.I.R. to have made an outstanding contribution to the research work of the department during the previous twelve months. Dr Essen's work on the establishment of an atomic frequency standard has extended over several years but the results published during the past year are regarded 'as the culmination of a brilliant series of researches'.

\* See *Research, Lond.* (1957) 10, 217; (1958) 11, 324

### Prevention of Skidding

The Road Research Laboratory have for some time been investigating the effect of road surfaces on skidding. More recently these investigations have been carried one stage further and the resistance to skidding of rubber tyres, differing both in composition and design, on slippery roads has been measured (see Table 2). The results of this work, together with that of Dr TABOR at Cambridge\*, led to what can only be called a fundamental discovery: when a wet rubber surface, or a greasy rubber surface, slides or rolls over hard spherical or conical bodies—and for this purpose the road surface may be considered to be composed of such bodies—a major part of the frictional resistance appears to be due to hysteresis losses in the rubber itself.

When rubber rolls or slides over a protuberance—as tyres do on roads, even apparently 'smooth' roads—a portion of the rubber is compressed so that work is done on the rubber. After it has passed the protuberance, it recovers elastically and, if the rubber were an ideal elastic body, the energy restored as the rubber recovers would be exactly equal to the work done in compression. In practice, however, no rubber is an ideal elastic body and when deformed some energy is lost by internal friction or hysteresis, the amount of energy lost depending on the composition of the rubber.

It is obvious, therefore, that a rubber with high hysteresis losses gives a greater frictional resistance and will reduce or prevent motor vehicles skidding on wet roads. There are, however, at least two adverse features to this solution. High energy losses within the tyre may cause overheating, softening of the material and eventually the tyre would burst. This effect can be considerably reduced by making the body of the tyre from a rubber possessing low hysteresis loss properties and only the tread of a material with high hysteresis losses.

If the tread is made from a material with high hysteresis losses, to give the desired frictional resistance on slippery roads, the free rolling friction will also be high. It is suggested that this undesirable effect can be reduced, to some extent at least by altering the geometry of the tyres to give a long narrow band of contact.

These results have not, of course, provided the answer to all the problems of tyre design but it now seems clear that if 'means can be found for using rubber with higher (hysteretic) losses in the treads of tyres . . . the gains should be considerable and, together with the progress already made in road surfacing, could go a long way indeed toward meeting the problem of skidding under wet conditions'†.

### Channel Tunnel

The idea of building a tunnel underneath the English Channel is by no means new. Serious work on the project was started in the 1870s but ceased after the shaft and pilot tunnels had been driven a short distance under the sea from both the French and British coasts. Recently an investigation of the possibility of driving such a tunnel has been undertaken by the Channel Tunnel Study Group which is composed of members from the English Channel Tunnel Company, the French Channel Tunnel Company, the Suez Canal Company and an American company, Technical Studies, Inc. (The Economist Intelligence Unit and the French company S.E.T.C. are assessing the economic factors affecting the driving of the tunnel and the results of their findings are still awaited.)

\* TABOR, D. *Engng* (1958) **186**, 838; GILES, C. G. and SABEY, H. E. *ibid.*, p. 840

† GLANVILLE, W. H. *James Forest Lecture* (Institute of Civil Engineers, 17th March, 1959)

Figure 3. Results of lock wheel braking tests on two wet surfaces—reproduced from *Engineering* (1958) **186**, 840

Test surface	Retardation measured with all wheels locked for one second at 30 m.p.h. on wet surface		
	Smooth tread tyres	Conventional patterned tread tyres	Patterned tread tyres with high hysteresis loss tread rubber
Smooth looking surface on which conventional tread patterns give a marked increase in skid resistance over smooth tyres	0.35g	0.63g	0.78g
Coarse textured surface with polished stone on which tread patterns give no increase in skid resistance compared to smooth tyres	0.35g	0.34g	0.67g

The Group has nearly completed a geological and geophysical investigation of the rock strata beneath the channel. Rock strata underneath the Channel are composed of three layers of chalk followed by gault clay and underneath this a belt of green sand filled with water which exerts a considerable upward pressure on the rock strata. The object of the study is to find a route where the lowest layer of chalk—the only layer really suitable for tunnelling—is fault-free and thick enough for safe operation.

Preliminary interpretation of the seismic and sonar soundings have shown remarkable agreement with the geological map drawn up in 1873. Other measures have included diamond drilling on both sides of the Channel to a depth of about 600 feet producing cores four and a half inches in diameter through the middle and lower chalk, gault and green sand formation. Samples of the sea bed have also been obtained by divers.

To confirm this survey, a British firm, George Wimpey & Co. Limited have been commissioned to obtain specimens of the rock strata for about 200 feet below the sea bed. Bore holes will be sunk from a floating craft, the *Ian Salvor III*, which eliminates the construction of expensive drilling platforms. The positions of the bore holes have been decided as a result of last year's geophysical survey and borings will be made by diamond drilling through a lining tube entered into the sea bed. (In rougher weather percussion methods may be used.) It is intended to remove six inch cores of rock for laboratory analysis. Water will also be pumped into the bore holes to test the absorption of water at various levels and when the tests have been completed the bore holes will be cement grouted to prevent water entering the rocks near the route finally chosen for the proposed tunnel.

### Mechanical Power from Liquid Gas

Both the engineer and the industrialist are always searching for new ways of producing cheaper and cheaper mechanical power. The idea that vapour from a liquified gas can be made to do mechanical work appears to have interesting possibilities. An invention has been patented\* which uses the vaporization of liquified gas to produce mechanical energy. The gas, in this particular case methane, is compressed in the liquid state to a pressure well above that required at the gas delivery point. A natural heating store such as the atmosphere or a river supplies heat to the liquid gas which will evaporate

at a temperature well below the ambient, and is then expanded in a turbine or reciprocating expander.

British Oxygen Research and Development Limited claim that the work required to compress the original liquid will only be a small fraction of that produced in the expansion engine and the balance will therefore be available as free mechanical power, suitable for such purposes as the production of electrical energy.

### B.C.U.R.A. Open Days

The British Coal Utilization Research Association celebrated its twenty-first birthday on April 22nd and to mark this event a variety of interesting work was put on show for the benefit of distinguished visitors, members and the press.

The coal industry is, of course, having a tough time at the moment. It is very much a buyers' market but as coal is the only natural raw material in the United Kingdom, it is very important to promote research into the best ways and means of using this valuable product. For the first time a tentative formula for the structure of coal has been put forward. This is the result of fundamental work carried out by the Association and it has shown that coal is a mixture of aromatic and hydrogenated aromatic rings. It is not, unfortunately, a polymer of the type like cellulose which can easily be broken down into its component groups and the structure thus analysed. If any polymeric structure can be assigned to it it is rather that of a large mass of aromatics linked by 'carbon' bridges. Any attempt at degradation such as mild oxidation has usually led to a fairly complete breakdown of the product giving simple materials like carboxylic acid and phthalic anhydride. Other work is proceeding on the reaction of coal with fluorine and chloro-fluorides to see if fluorinated oils with specific properties can be obtained and some of the products produced so far do differ from those resulting from the fluorination of petroleum products.

The exhibit that was perhaps of most interest to all the visitors was the work of B.C.U.R.A. on the gasification of low grade coal. The important point about this work is that studies have been made on the temperature/viscosity characteristics of the slag and the results of these investigations have made it possible to tap off the slag continuously, from the fuel while the slag is still in liquid form. The slag falls into a water stream, flowing horizontally at high velocity, where it granulates and this granulated slag can then be separated from the water which is re-circulated.

\* British Oxygen Research and Development Limited *Brit. Pat. Specification 808,535*

# BOOK REVIEWS

## The Physical Theory of Neutron Chain Reactors

A. M. WEINBERG and E. P. WIGNER

(xii+800 pp; 9½ in. by 6 in.)

Chicago: University of Chicago Press; London: Cambridge University Press. \$15.00, 112s 6d

THE aim of the authors of the volume under review was to write a book on the physics of chain reacting neutron systems and to present the material in a scholarly fashion such as one could perhaps visualize a professor in a high class university would endeavour to present the subject matter. One can hardly imagine authors more suited to this task than Professor E. P. WIGNER of the Palmer Physical Laboratory, Princeton, and Dr A. M. WEINBERG, Director of the Oak Ridge National Laboratory. Professor Wigner is most distinguished by his work on nuclear theory and he and Dr Weinberg were active research workers in reactor theory from the beginning.

In accord with the aim, an excellent survey is given of the theories of nuclear reactions of importance to reactors. It is a masterly exposition, astonishingly easy to read, but full of rewarding insights into our present ideas of nuclear structure and reactions. In this first chapter (139 pages) the energy field covered is very wide, including shell structure, giant resonances, complex potential; it is also made clear that we do not, in fact, understand the basic fission process as yet. It astonishes the reviewer, however, that the rotational states provided by the Bohr-Mottelson model are not included, since they contribute to inelastic scattering in cases such as uranium 238.

The rest of the book (pages 140 to 800) comprises transport theory of neutrons, general reactor theory, heterogeneous reactors: in short, all that a professional reactor physicist will wish to know provided he is not frightened by Boltzmann's equation. Fortunately, all is expressed with great didactic skill and unusual clarity, with the extra helping word to make study easier.

The Weinberg-Wigner volume will no doubt be the basic text on the nuclear physics of reactors for many years to come. Most of the theory of reactors and a great deal of the purely nuclear section will be permanent; at a price of 1-875 cents per page the volume is price worthy. E. BRETSCHER

## Optical Properties of Semi-Conductors

T. S. MOSS

(x+279 pp; 8½ in. by 6 in.)

London: Butterworths Scientific Publications.  
New York: Academic Press. 50s

THIS monograph, one of a series dealing with special topics in the semiconductor field, is an extension of the author's earlier work on photoconductivity. The first part of the book, which forms about forty per cent of the whole, gives a theoretical treatment of the optical properties of conducting media, covering absorption and emission processes, inter-relation of optical constants, magneto-optic effects and photoeffects. This section is

likely to be of particular value to students and research workers, covering as it does in one consistent treatment the whole field from Maxwell's equations to the quantum mechanical description of optical absorption, cyclotron resonance phenomena and radiation emission processes.

The second part of the book is devoted to an account of the observed optical properties of many semiconductors and is perhaps more open to criticism. Inevitably the section is in a sense only a catalogue of published work in the field but, as is essential in a good book of this type, the catalogue is extremely comprehensive and unusually up to date (work as late as August 1958 is included). However it is felt that much of the data for the less well developed semiconductors, those other than Si, Ge, and InSb, would be more valuable if it were accompanied by details of the chemical purity and physical perfection of the samples being studied. As an example, in the discussion on the 'chalcogenides' of Zn, Cd, and Hg many workers are quoted as having observed various absorption lines or peaks in photo-spectra, but no collateral information on impurity concentrations is given. This is likely to reduce the value of the data, particularly to those engaged in the commercial development of comparable devices. These workers, too, will find some surprising omissions. The Ge phototransistor must today be one of the most commonly used semiconductor photodevices but nowhere is this device mentioned nor indeed is the simple Ge photodiode or any discussion of the relative behaviour in practice of one, two, or three element photodevices. It is also unexpected to find low temperature photoeffects in InSb dismissed so shortly since published figures suggest that these may be the basis for cells rivaling commercial PbTe cells in sensitivity with improved spectral response and time constant.

Apart from this type of omission, however, this book is a most valuable addition to textbooks on semiconductors and at the moment of writing may indeed be unique in that no other work covers this field so comprehensively and exclusively. D. G. AVERY

## The Structure and Evolution of the Universe

G. J. WHITROW

(212 pp; 8½ in. by 5½ in.)

London: Hutchinson. 21s

ONE of the purposes of building a better and a bigger instrument than ever before is to observe phenomena and events that you did not know were there. The large 200-inch telescope on Mount Palomar and the 250-foot radio telescope at Jodrell Bank were both built as a rational exercise. That is there were sound and predictable reasons for extending the depths to which we could survey the universe. But the exciting consequences have been those which were not foreseen. These consequences provide the primary reasons why there is such a ferment of ideas and speculation around the age old problem of the structure and evolution of the universe. Dr WHITROW's book is not merely a new edition of his earlier one entitled *The Structure of the Universe*. It is in effect a

new book and it provides an authoritative and well written introduction which surveys the universe as we have come to know of it. It is difficult to imagine that anyone would not find it stimulating, instructive and exciting.

G.K.T.C.

### Extensive Air Showers

W. GALBRAITH

(xvi + 211 pp; 8½ in. by 5½ in.)

London: Butterworths Scientific Publications;

New York: Academic. 40s, \$7.50

THIS book is concerned with the study of the ultra high energy component of the cosmic radiation. Single primary particles of energy  $10^{14}$  to  $10^{17}$  eV suffer successive collisions in traversing the earth's atmosphere, and generate a mixed cascade of nucleons, mesons and electrons, so producing the so-called extensive showers, containing typically a few million particles spread out over a hundred or so square metres at sea level. Although such showers were first observed some twenty years ago, Dr GALBRAITH's book represents one of the few attempts to present a coherent account of the work in this field of research, in a form readily comprehensible to the non-specialist.

Since the extensive showers represent the end product of a complex cascade process propagated through  $1000 \text{ g/cm}^2$  of atmosphere, it is of course difficult, from observations at sea level or moderate altitudes, to extrapolate back to determine the characteristics of the first energetic collision: various measureable quantities, such as the lateral distribution in numbers and types of particles, and their variations with altitude or depth below ground, must be compared with the different theoretical models in the hope that one of them may give an adequate account of the data. The first six chapters of the book are devoted to an analysis and discussion of such results. One criticism which one can make of this analysis is that little attempt has been made to formulate a clear statement of the main conclusions which follow from the mass of observational data, and their theoretical interpretation.

The remaining two chapters are concerned with the cosmological aspects of the work on extensive showers. At very high energies, the radius of curvature of primary particles in the galactic magnetic fields becomes comparable with the dimensions of the galaxy itself; one might then expect anisotropies which would be revealed as time variations in the rate of discharge of the detecting apparatus as it points to different regions of the sky. The author discusses these very important experiments, and also those designed to detect point sources of cosmic rays, in some detail.

The book is essentially written from the point of view of an experimentalist, by an author who has himself done prominent work in this field. The main results

following from the theoretical treatment of air-showers are clearly stated, but mathematical elaboration has been kept to a minimum. The description of the experimental apparatus and methods employed, though necessarily brief, is entirely adequate for full understanding of the principal physical problems involved in this type of research.

The book is particularly timely, for it comes at the end of a quarter century epoch, during which cosmic ray studies were concerned to a great extent with the many new types of elementary particles first observed in this field. Now that such particles can be better investigated by means of the large accelerators now operating or under construction, the emphasis in the cosmic ray field has shifted to studies of the primary radiation and to the ultra high energy component of the spectrum.

D. H. PERKINS

### Radiation Protection

(18 pp; 9½ in. by 7½ in.)

London: Pergamon Press (for the International Commission on Radiological Protection). 3s 6d

THE recommendations of the International Commission on Radiological Protection which were adopted on September 9th, 1958 are clearly set out in this booklet. The recommendations state the basic concepts of radiation protection: their objectives, types of exposure, reduction in maximum permissible dose and the time interval over which a dose must be assessed. Under the heading of maximum permissible doses consideration is given to the effect of exposure on individuals, such as occupational exposure or accidental high exposure, and the exposure of whole population groups where an overall genetic effect might be expected. Recommendations are also given with regard to working conditions.

### Nomenclature of Inorganic Chemistry 1957

(ix + 93 pp; 10 in. by 6½ in.)

London: Butterworths Scientific Publications. 15s

THIS small book contains all the rules and recommendations for the nomenclature of inorganic chemistry which were adopted by the International Union of Pure and Applied Chemistry as a result of a report by the Commission on the Nomenclature of Inorganic Chemistry, dated 1957. It deals with names and symbols used for elements and groups of elements, the formulae and names for compounds in general, names for ions and radicals and for crystalline phases of variable composition. The correct naming of acids, salts and salt-like compounds is also set out.

The booklet is printed both in French and in English and forms a companion to *Nomenclature of Organic Chemistry 1957* published by Butterworths Scientific Publications at the end of 1958.

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